Electrochemical Impedance Spectroscopic Study of Polythiophenes on Carbon Materials

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This review article focuses on electrochemical impedance spectro-scopic study of thiophenes on carbon materials, the importance of which has been realized by recent progress in literature. The review article has 3 separate sections. In the first part, most of the thiophene derivatives (thiophene, 3-methylthiphene, 3-hexylthiophene, 3,4-ethylenedioxythiophene, 3,4-propylenedioxythiophene, bithiophene, octylthiophene, 3-dodecylthiophene, 3-terthiophene, 3-phenylthio-phene, 3-methoxythiophene) and copolymers of thiophenes have been reviewed. In the second part, carbon surfaces (carbon fiber micro-electrode, glassy carbon, carbon nanotubes, etc.) were used as effec-tive electrode materials. In the third part, the electrochemical impedance spectroscopy (EIS) of thiophenes was explained with supercapacitors and many different circuit modeling evaluations.

Keywords Circuit models; Coatings; Electrical properties; Electrochemical properties; Thin films; Polythio-phenes

INTRODUCTION

Although conducting polymers have received consider-able attention, there is still much to be learned about their structure and properties. One approach to understand the behavior of complex polymeric materials is to prepare and study oligomeric analogues. Conducting polymers (CPs) are usually composed from partially oxidized or reduced parts, and they are highly conjugated π-systems. The characterization of the oxidized or reduced oligomer in sol-ution, properties of the solid ionic oligomer can help in the understanding of the conducting polymers, but there are still difficulties in explaining the intramolecular effects from the intermolecular effects present in solids[1]. Most of the π-conjugated polymers are straightforwardly prepared by chemical and/or electrochemical methods and their electronic properties can be reversibly charged between insulating and conducting states by chemical and/or electrochemical doping reactions[2].

Among these numerous CPs, poly(thiophenes) (PTs) and derivatives have rapidly become the subject of considerable interest for supercapacitor and biosensor applications for more two decades[3]. Polythiophene and its derivatives can be electrochemically deposited[4–7], constituting a potentially simple process for device prep-aration. Among the various possible strategies for modifi-cation of CPs, the polymerization of monomers with functional groups represents the most straightforward method to achieve a molecular level control of the structure and electronic and electrochemical properties of functional CPs[8].

Poly(Thiophene)

Polythiophene, as a representative of the conducting polymers, has received great scientific attention in the last 20 years, not only owing to its interesting properties (good environmental and thermal stability), but also owing to the wide application perspectives[9]. Numerous polyalkyl derivatives of thiophene have been synthesized so far by chemical and electrochemical approaches, resulting in con-ducting polymers with better solubility and very interesting properties[10].

Generally, the electrosynthesis of PT and its derivatives was performed on noble metals like Pt and Au in an organic medium such as acetonitrile, propylene carbonate or nitro-methane[11]. Some less noble metals, such as Al, Fe, and Zn have been recently reported as electrode mate-rials for electrochemical polymerization of Thiophene in dichloromethane[12]. Wang et al.[13] have reported that PT films could be also grafted on relatively reactive metals like copper from BF_3-diethyl ether solution[14]. The introduc-tion of titanium electrodes is especially important in polymer electrochemistry due to their wide working potential window when compared to many others.

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Due to their unique electrical properties and their environmental stability, polythiophenes have shown considerable promise for materials applications[15–17]. However, the high oxidation potential of thiophene compared to the polymer causes some degradation of the polymeric film. Recently, this problem was overcome by extending the conjugation length of the monomer, resulting in a significant reduction in the oxidation potential, while still producing polymers with high conductivity, good electrochemical properties and thermal stability in the oxidized state[18,19].

Thiophene derivatives have been found to exhibit a wide range of biological activities[20], and many thiophene derivatives are active compounds as chemotherapeutics[21], while they have also been in various materials science applications[22]. PTs obtained both chemically and electrochemically display interesting optical and charge transport properties. Variation of substituent geometries and shapes has provided detailed insights into the structure-activity relationships and have been scrutinized in several excellent reviews[23,24].

Polythiophene and its derivatives have been widely studied during the past years, owing to their large application possibilities[25], including sensor and/or biosensor[26,27], electrochemical[28,29] and photovoltaic cells[30,31], energy storage[32,33], transistor[34,35], electroluminescent diodes[36], or protective coatings[37,38]. PTs have shown considerable promise for materials applications, due to exceptional electrical properties and their environmental stability[39–41]. However, the high oxidation potential of thiophene compared to the polymer causes some degradation of the polymeric film, which has been the subject of a wide variety of studies.

Much of the research on molecular electronics and non-linear optics are an objective of numerous considerations[42–46]. Much of the research on this area has been addressed to conjugated thiophene oligomers[47–50], formation[51,52] of ordered mono-layers in self assembly process[53], chains interactions[54], and π-stacks[55].

A new conjugated polymer combining in its structure thiophene rings and nitrogen containing heterocycles, poly[2,3-di(2-thienyl) quinoxaline], with electrochemical methods using different experimental conditions was synthesized by Diaz et al. The monomer was electrochemically characterized. Theoretical calculations of global and local reactivity index such as frontier orbitals energy gap and Fukui functions present a good consistency with the experimental results[56].

For most electrophilic substitution reactions, thiophene exhibits similar reactivity to benzene. However, the primary exception to this is the nitration of thiophene, where most standard nitration conditions result in violent, uncontrollable reactions and little formation of the nitro products[57–59].

Niemantsverdriet et al.[60] have studied the thiophene hydrodesulphurization (HDS) activity of unpromoted and Ni-promoted Mo model catalysts supported on various substrates. Combining these results with activity measurements and angle dependent XPS on Ti-promoted Mo catalysts, authors concluded that Ti species can act as in the case of Co or Ni.

Furthermore, sulfide Ti-species increase the hydrogenation activity as evidenced by relatively higher amounts of butane after thiophene HDS. Mousava et al.[61] studied with the polythiophene modified glassy carbon electrode to be used the determination of metal ions such as Cu(II), Pb(II), Cd(II) and Zn(II) by differential pulse anodic stripping voltammetry.

A compound of thiophene with a mesogen group in position 3 of the ring (4'-8-thiophen-3-yl-octyloxy) biphenyl-4-carbonitrile) has been reported that some mesophases could be identified. Electropolymerization was also attempted, but difficulties in the characterization of the polymeric material were found because the biphenyl group is also electro-active[62]. Ethyl 2-amino 4,5,6,7-tetrahydro-benzo thiophene-3-carboxylate maleimide (ETTCM) has been synthesized and investigated as a new thio-maleimide derivative[63]. The synthesis of group (I) and group (II) hydrochloric acid doped homopolymers and copolymers such as poly(aniline-co-thiophene) were investigated via chemical oxidation process using ammonium and potassiumpersulphate as chemical initiators[64].

Poly(3-methylthiophene)

Poly(3-methylthiophene) (P3MT) and its derivatives have attracted considerable attention over the past 20 years, mainly because of their remarkable solid-state properties including thermochromism, luminescence and photoconductivity[65]. Mazur have demonstrated electroless deposition of P3MT on a number of substrates, ranging from noble metals to polycarbonate (PC) membranes[66]. Poly(3-methylthiophene) has been synthesized by the chemical oxidation polymerization method using FeCl$_3$[67].

A reversible cyclic voltammogram is generally only observed whether both the oxidized and reduced species are stable and the kinetic of the electron transfer process is fast. The fast kinetics might be related to template synthesis, decreasing the defects along the poly(3-methyl thiophene) chain, thus improving the electronic and ionic conductivity. The diffusion coefficient was determined using the Randles-Sevčik equation[68]. The values obtained for the anodic and cathodic current peaks were very similar (1.2×10^{-9} cm^2 s^{-1} and 9.1×10^{-10} cm^2 s^{-1}, respectively) (Fig. 1a). In the case of n-doping, the irreversible behavior was verified in Figure 1b, the inset showing the transition from reversible to irreversible behavior with increase of the sweep rate[69].

Cyclo voltammetric and electrochemical impedance spectroscopic studies clearly revealed the existence of high capacitance behavior for polythiophene in the initial monomer concentration of 0.5 M ($C_{LF} = 1.13\,F\,g^{-1}$ compared to poly(2-methylthiophene) in the initial monomer concentration of 0.2 M ($C_{LF} = 6.35\,mFg^{-1}$) thin film coating on the carbon fiber microelectrode (CFME)[70].

Balducci et al. have studied a long cycle - life, high voltage supercapacitor featuring an activated carbon/P3MT hybrid configuration with *N*-butyl-*N*-methylpyrrolidinum bis(trifluoromethanesulfonyl)[71]. The presence of alkyl groups at the 3-position of the thiophene unit affords a series of highly conductive and processable poly(alkylthio-phene)s[72]. Due to steric interactions between the alkyl substituents, in his study Roncali[73] suggested a large number of twisted thiophene rings that were out of conjugation. However, Tashiro et al.[74] have shown that the increase in the length as the alkyl side chain increases as a result of enhanced inter-molecular interactions between the longer alkyl groups.

Poly(pyrrole) and poly(3-methylthiophene) were uniformly deposited onto multiwalled carbon nanotubes in an organic system by chemical methods. Xiao et al. have studied[75] a carbon nanotube polypyrrole composite and poly(3-methylthiophene)-based supercapacitor prototype (CNTs-PPy-CNTs-pMeT SCP), a carbon nanotubes-carbon nanotubes-polypyrrole-based hybrid SCP (CNTs-CNTs-pPy SCP), as well as a CNTs-CNTs corresponding SCP assembled in 1 M LiClO$_4$/acetonitrile. They studied their voltammetry characteristics, galvanostatic discharge and AC impedance spectra, in two-electrode mode. Pseudo-capacitance effects have been found from those SCPs with composite electrodes, and capacitances have been found to be 87, 45 and 72 F g^{-1} for CNTs-pPy-CNTs-pMeT SCP, CNTs-CNTs-pMeT SCP and CNTs-CNTs-pPy SCP, respectively.

The scanning electron microscopy (SEM) picture of the solution side of a 200 ^{0}A-thick film of P3MT was shown in Figure 2a, the surface is typical for undoped P3MT films. In this figure, the surface looks homogeneous and shows some roughness due to the platinum substrate and relatively thin film. The compactness of the structure is attributed partially to the removal of the dopant anions and to conformational changes due to polymer chain rearrangement. Figure 2b shows the SEM of a P3MT/sol-gel copper phthalocyanine (CuPc) film.

In this case, the surface appears to have more amorphous structures. This is attributed to the deposition of the inorganic moiety over the conducting polymer layer. At this level of magnification, no pores were identified; however, different packing distributions of the film are noticed. The surface shows relatively higher homogeneity compared to the P3MT unmodified film. Due to the effect of blending caused by heating, the surface is also shown with some particles appearing sub-wigged into the film. A defect in the surface caused by the mount of the SEM holder is noticed at the upper left corner of the picture[76].

The oxidative p-doping of polymers like polypyrrole, polythiophenes and derivatives, if conducted in the presence of nucleophilic species, can be suitable as a valid synthetic approach for the derivation of conducting polymers, subsequent to their polymerization.
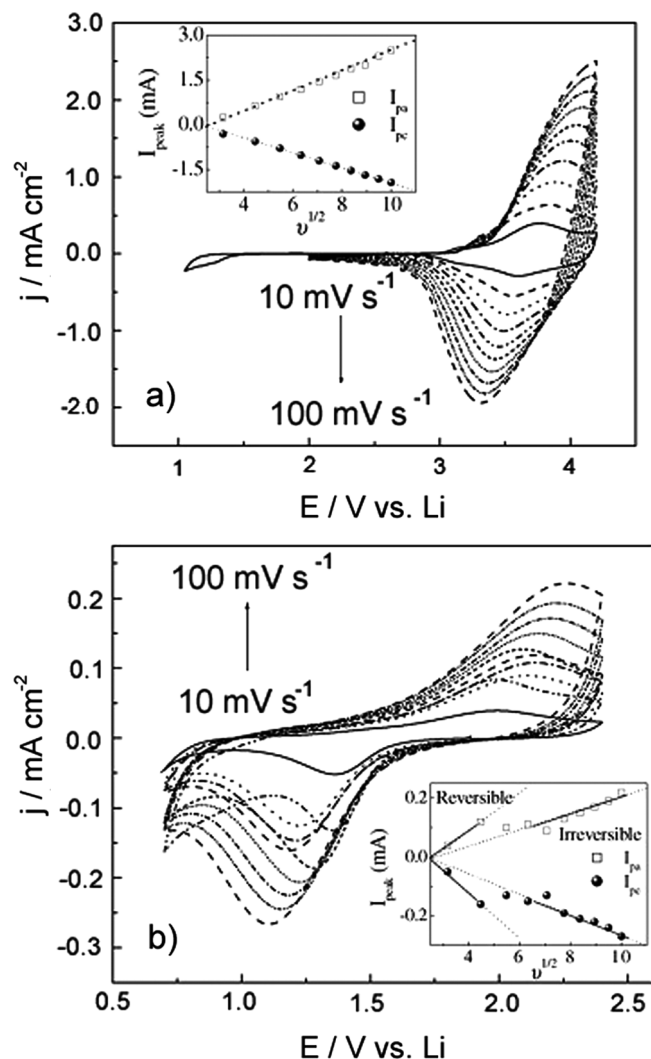

FIG. 1.   Cyclic voltammetry of the P(3MT)/PVDF | PC/EC/1 molL-1 LiClO$_4$ | Li system at several scan rates for a) p-doping and b) n-doping. Inset shows a plot of the dependence of the peak current density on the square root of the potential sweep rate. Reprinted from Ref. [69]. Fonseca, C.P.; Benedetti, J.E.; Neves, S. J. Power Sources **2006**, *158*, 789–794.

Poly(3-hexylthiophene)

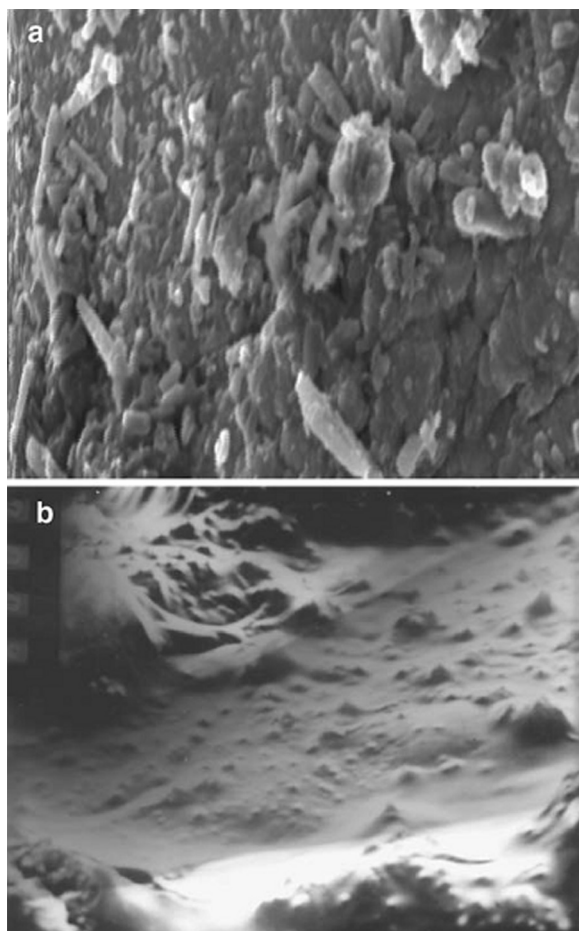Substitution of an alkyl chain at the 3-position of the thiophene monomer makes poly(3-hexylthiophene)

FIG. 2. (a) SEM for P(3MT) over Pt electrode ($E_{app} = 1.8$ V for 20 s; magnification $\times$ 1.500; thickness of the layer 200⁰A, b) SEM for P(3MT) modified with Cu-phtalecyanide sol-gel (magnification $\times$ 1.500). Reprinted from Ref. [76]. Galal, A.; Darwish, S.A.; Ahmed, R.A. J. Solid State Electrochem. **2007**, *11*, 531–542.

(P3HT) soluble in many common organic solvent, e.g., xylene, tetrahydrofuran, and dichlorobenzene. Spin or drop casting of such P3HT solution allows for the easy fabrication into thin films and devices for studies of the electronic and the optical properties of the polymer[77]. Mark et al.[78] have synthesized soluble conducting polymers of 3-hexylthiophene, 3-octylthiophene, 3-decylthiophene and 3-dodecylthiophene by constant potential electrolysis.

They studied molecular weights with gel permeation chromatography on solutions of the polymers in toluene. Surface properties were investigated by SEM. Substituent groups lengths have been found to strongly influence the electronic properties of the resultant polymers. Poly(3-hexylthiophene) has shown the highest conductivity, with the highest degree of polymerization. The conductivity and the degree of polymerization values decrease as the substituent chain length increases.

Sirringhaus et al.[79] have demonstrated the high charge-carrier mobility of polymer field-effect transistors (FETs) through two dimensional charge transport. In Sirringhaus's work, supra-molecular self-organization in poly(3-hexylthiophene) (P3HT) played an important role in enhancing charge transport in conjugated polymer semiconductors. Supra-molecular self-organization in poly(3-hexylthiophene) (P3HT) played an important role in enhancing charge transport in conjugated polymer semiconductors.

The mobility enhancement in conjugated of polymer field-effect transistors (FETs) through chain alignment was also achieved in a liquid-crystalline (LC) copolymer, poly(9,9'-N-dioctylfluorene-alt-bithiophene). The microstructure of the nematic conjugated polymers could be controlled by LC self-organization with the help of an additional alignment layer. Furthermore, fluorine-based polymers have better stability than thiophene-based homopolymers such as P3HT because of their rigid structures and lower highest occupied molecular orbital levels.

Poly(3,4-ethylenedioxythiophene)

Poly(3,4-ethylenedioxythiophene), (PEDOT) has become one of the most attractive conductive polymers due to its high electrical conductivity transparency and structural stability[80,81]. As a consequence of its excellent properties, PEDOT is being used in a great number of traditional and emerging applications including antistatic coatings, light emitting diodes, capacitors, electro-chromic, photovoltaic and sensor devices[82]. To diversify the properties and expand the functions of these classical π-conjugated polymers, the incorporation of hetero-atoms into the conjugated chain, is expected to produce interesting properties[83].

PEDOT belongs to the class of conducting polymers of thiophene series. Increased interest to it is caused by the highly stable electrochemical responses of the film, its interesting electric and optical properties, which one of practical importance for different fields of science and engineering. In particular, PEDOT is proposed as a material for the development of power storage devices, such as supercapacitors or galvanic cells (batteries, secondary cells)[84,85] and also as anticorrosion and antistatic coatings, electrochromic devices, and biosensors[86–88]. Introduction of a cyclic substituent with electron-donating oxygen atoms in positions 3 and 4 results in the decrease of the oxidation potential and assists the formation of polymer with a more regular structure[89–91].

PEDOT exhibits many favorable properties, including a low band gap (1.6 eV) and oxidation potential for conversion to the conducting state and high stability in the conducting form[92]. However, the poor solubility of poly(3,4-ethylenedioxythiophene)s is a strong drawback for further applications in electrical and optical devices.

To solve these problems, a PEDOT derivatives, poly(3',3'-diheptyl-3,4-propylenedioxythiophene) and poly(hepthyl$_2$-PEDOT), show good solubility in most of the common organic solvents[93]. 3,6 bis (3,4-ethylenedioxythiophenyl)-9-ethylcarbazole was synthesized by Stille coupling instead of Grignard coupling, as reported before for *N*-methyl derivative[94], and the determination of the optimum conditions for preparation of an electro-active polymer on carbon fiber (CF) was reported in literature[95].

In previous studies, Buhimann et al.[96] have shown that the doping ion used in the fabrication of PEDOT-based sensors has an important effect on the analytical performance of the sensors. As a ''soft metal'', Ag$^+$ interacts with sulfur atoms and double bonds (π-coordination)[97]. Ag$^+$-Ion selective electrodes (ISEs) based on PEDOT doped with a compound containing sulfonate groups and/or double bonds[98,99] show better sensitivity to Ag$^+$ than sensors based on PEDOT doped only with a weakly coordinating anion, such as hexabromocarborane[100].

PEDOT has been much more investigated compared to majority of conducting polymers due to its exceptional electrochemical properties and unusual thermal stability in oxidized state[101,102], and due to its high conductivity make it useful as conducting electrode in electrochemical supercapacitors[103–105]. Poly(alkylbithiazoles) exhibit interesting thermo-chromic and electrochemical behavior[106–108] especially nonyl derivative shows unusual optical properties as a result of its crystallinity and π-π stacking behavior. The π-stacking of thiazole rings between neighboring chains and increased planarity along the backbone causes well ordered polymer films[109–112].

Poly(3,4-propylenedioxythiophene)

Besides PEDOT, other poly(3,4-alkylenedioxy thiophenes) and their derivatives also show very interesting electronic, electrochromic and optical properties[113]. A dibenzyl substituted poly(3,4 propylenedioxythiophene) has been synthesized which is found to exhibit 89% electrochromic contrast in the visible region with faster switching time[114]. The processability and functionalization of poly(3,4-alkylenedioxythiophene)s and their derivatives has always been a challenge due to insolubility of the polymers[115]. Mishra et al.[116] have successfully designed and synthesized mono and symmetric disubstituted 3,4-propylenedioxythiophenes in order to get soluble and processable polymers.

Multiwalled carbon nanotubes (MWNTs) were functionalized with poly(3,4-propylenedioxythiophene) (PProDOT) using a simple ''chemical grafting'' approach. After the conventional acid oxidation (AO) process, the MWNT-COOH was converted to the acyl chloride functionalized MWNTs (MWNT-COCl) by treating them with thionyl chloride. The MWNT-COCl were further reacted with a functionalized monomer based on 3,

4-propylenedioxythiophene (ProDOT-OH), followed by oxidative polymerization to prepare the MWNT-g-ProDOT hybrid. ProDOT-OH can be controllably synthesized in a single step[117].

Dietrich et al.[118] first reported that the conjugated polymers from ProDOT exhibit higher contrast in comparison to polymers from EDOT. The difference between ProDOT and EDOT is one extra methylene group in the cyclic structure. Based on this finding, very recently, Kumar and coworkers[119] have shown that polymers based on ProDOT are processable and highly efficient electrochromic materials. These materials are shown to have promising applications in optical materials, smart windows, and electrochromic displays. Moreover, the monomer functionalized MWNTs were further copolymerized with thiophene to prepare tubular nanostructures coated with conducting copolymers on CNTs (MWNT-g-PProDOT-co-PTh).

Poly(Bithiophene)

Among conducting polymers, polybithiophene (PBT) attracted considerable interest owing to its easier electrosynthesis: the oxidation potential of the monomer is lower than those of unsubstituted or 3-methyl-substituted thiophenes. PBT has already been obtained on Pt in organic[120,121] and in micellar media[122,123] on Pt and oxidizable metals such as Fe, Al or Ti[124]. The use of micellar media (especially anionic ones) leads to more homogenous and regular structures[125,126].

It has been observed that polythiophenes obtained from galvanostatic polymerization of thiophene, bithiophene, and terthiophene in 0.5 M LiClO$_4$ in propylene carbonate present different conformation, depending on the starting compound. Bithiophene was cited as an excellent candidate for the preparation of high quality polythiophene[127–129] and highly smooth and neutral polythiophene prepared by electropolymerization of bithiophene was also successfully used as a hole injection contact in molecular light-emitting diodes[130].

These electrochemical characterizations of PBT films in aqueous LiClO$_4$ solutions showed dissymmetric oxidation and reduction peaks, describing the doping/undoping processes[131]. EIS has been used to study polyoctylthiophene films in an organic medium[132], poly(3,4-ethylenedioxythiophene)[133], and polybithiophene films[134] in aqueous media[135].

A study of the cathodic and anodic doping of polybithiophene and poly(3-phenylthiophene) in acetonitrile and propylene carbonate demonstrates that the main fractions of changes of either sign undergo quasi-reversible redox conversions. Two types of retarted processes reveal themselves. One is associated with conversions of residual portions of positive and negative doping changes trapped in the non-conducting matrix of a neutral polymer at final stages of the undoping process. The other is due to redox

conversions of polymer chemically modified when interacting with solution components[136].

Giannetto et al.[137] have demonstrated how the electrochemically induced substitution at the 3/4- position of galvanostatically synthesized poly(2, 2′-bithiophene) can be easily obtained by potentiostatic or potentiodynamic (cyclic voltammetry, (CV)) methods under strict control of the experimental parameters; the study was focused on electrochemically induced alkyoxylation, conducted by employing two primary alcohols (2-chloroethanol and 2-bromoethanol) and a secondary alcohol (1-bromo, 2-propanol) as model synthesis.

Poly[4,4′-bis(alkylsulphonyl)-2,2′-bithiophene]s (PRST) bearing short-chain substituents, such as methyl, butyl, and 2-methylbutyl as the alkyl groups, Seeber's et al. have attracted[138] attention due to: 1) the repeatable responses obtained; 2) the particular stability; 3) the good definition and resolution of the signals due to polaron and bipolaron formation; 4) the relatively easy reduction leading to n-doping, and the consequent reduced band gap. In Seeber's previous papers[139–141] repeatable and reliable data have been obtained in studies on the influence of the nature of the anions present on the anodic electrodeposition and on the electrochemical properties of PRSTs[142,143], in the characterization of the electro-generated coating by faradaic impedance measurements[144,145].

Poly(Octylthiophene)

In addition to functional properties of the thiophene ring, another concept widely accepted to modify PT properties is the copolymerization process with different alkyl substituted thiophenes. The formation of a copolymer has been a common approach to material with tailored properties. Earlier reports on chemically and electrochemically generated copolymer have appeared for thiophene and its alkyl derivatives. For example, copolymerization of thiophene with 3-methyl or 3-octylthiophene[146,147], as well as large number of copolymers based on 3-alkyl substituted derivatives, i.e., 3-methyl/3-octylthiophene[148,149], etc., but the solubility as a very important characteristic was still very limited.

Buzarovska et al.[150] have made a comparative investigation of the electrochemical response of poly(alkyl thiophene) derivatives (3-methylthiophene and 3-octylthiophene) on two different electrode materials (platinum and titanium) was performed using cyclic voltammetry. By analyzing the voltammetric data, a slight potential shift of the oxido-reduction peaks in poly(octylthiophene) film deposited on titanium electrode compared to platinum has been observed. The calculated surface concentrations of the electro-active centers were found to decrease significantly in poly(octylthiophene) grafted onto titanium surface, whereas, in poly(methylthiophene) these changes were negligible.

The influence of the nature of the electrode material and the alkyl substituent length on the redox properties has been discussed. The reduced forms of the synthesized polymer films were characterized by FTIR spectroscopy. The FTIR spectra indicate decrease of the conjugation length, the degree of polymerization and the presence of defects (2, 4 linkages and C=O groups) with the increase of the alkyl group length. Plieth et al.[151] have studied the synthesis and characterization of some homo/co-oligomers is based on thiophene, 3-methyl, and 3-octylthiophene. Functionalization of the thiophene unit by 3-alkyl substituents (methyl and octyl) leads to lowering of the effective conjugation lengths, and therefore results in lower thermal stability of the samples. The presence of thiophene in the corresponding cooligomers improves the stability of the material. In contrast, the possible defects (C=O groups or 2, 4-linkages) were more pronounced for temperature and the cooligomers with a higher proportion of thiophene, meaning a shortening of the conjugation length. The observed behavior was mainly governed by steric reasons.

So far, as data in the literature, one should expect that altering the length of the chain of the alkyl substituent in position 3 of the thiophene ring, especially, transition from 3-methylthiophene to 3-octylthiophene will lead to a change in the film structure, its morphology. Actually, despite similar structure, substantial differences are observed in the microstructure of such films. Tourillon et al. have electro-synthesized poly(3-methylthiophene) films, exhibiting a fibrillar microstructure with a random arrangement of fibers. In contrast, poly(3-octylthiophene) films according to X-ray diffraction (XRD) data[152] are characterized by predominance of ordered orientation of chains in space without any twisting, leading to the formation of layered structures, where there takes place a coplanar arrangement of thiophene rings with a considerable manufacturing effect.

Thiophene structures anchored in position 3 of the ring were synthesized using spacers of different lengths (6, 8, 10 and 12 carbon atoms linked to a 2-((4-octyl-phenylimino) methyl) phenol) group. The thermal studies of the units demonstrated that they possess liquid-crystal properties and their optical study indicated that all the compounds present a nematic phase. Further chemical polymerization of these units was performed by oxidation of the respective monomers using iron (III) chloride. The resulting polymers proved to be insoluble and therefore their characterization was only possible by X-ray photoelectron spectroscopy (XPS) and Fourier Transform Infrared – Attenuated Total Reflectance (FTIR-ATR) techniques[153].

Lapkowski et al.[154] have investigated electrochemical and related aspects, like doping process of a series of α-monochloro-substituted regioregular (3-octylthiophene) oligomers recently[155–157]. Bobacka et al.[158] have studied with Poly(octylthiophene) (POT). The film is obtained after

it is covered within aqueous solution. Electropolymerization is usually performed in the presence of $LiBF_4$ or tetrabutyl ammonium perchlorate (both in propylene carbonate solutions). Li^+, Ca^{+2} and Cl^- selective electrodes have been obtained with a poly(octylthiophene) transducer. All of the electrodes obtained show increased stability (potential drifts for the Ca^{+2} sensor were in the range of $0.23\,mV/day$ to $-1\,mV/day$, depending on the substrate used) over a coated-wire arrangement tested in parallel (potential drifts of the Ca^{+2}–selective coated wire electrode were in the range of $-3.8\,mV/day$ to $-5.0\,mV/day$, depending on the substrate used). The most stable sensors were produced when glassy carbon (GC) substrate was used.

Poly(3-dodecylthiophene)

Poly(3-alkythiophene)s (P3ATs) with various side chain lengths (C_nH_{2n+1}) ranging from 4 to 8 exhibited good solubility and fusibility, and have been extensively studied[159]. Among poly(3-alkythiophene)s poly(3-dodecylthiophene) (P3DT) with 12 carbon atoms in the side chain exhibited good electric conductivity, thermochromism and solubility[160]. Cik et al.[161] have studied that the influence of the heat-induced conformational changes are in side alkyls and in the backbone of poly(3-dodecylthiophene) (PDDT) is a higher content of configurational head to head defects (39%) on electronic conductivity. It has been found that conformational changes affect the electric conductivity values of PDDT doped with $FeCl_3$ attaining at $0.021\,mol$ of Fe/mol dodecylthiophene more than $108\,S\,m^{-1}$ within the whole temperature range (from 78 up to 320 K).

Prosa et al. have studied that conformational changes in the (semi)crystalline cell of poly(3-dodecylthiophene) with temperature ranging from -130 to $125°C$ (143 to 398 K) were characterized by the XRD method[162] and by the application of molecular dynamics and diffraction simulation[163]. These studies have shown that up to approx. $25°C$ (298 K) the unit cell structures of PDDT are similar (insignificant changes of a parameter and no changes of inter-planar backbone b-parameter in the orthorhombic cell). That means the X-ray diffraction studies have not provided adequate information about the conformational changes of polymer chains below room temperature. However, as temperature increases, content on alkyl side chains also increases.

Poly(Terthiophene)

Polythiophenes are for use in photovoltaic devices since it is easier for a wide variety of substituents to be covalently attached to the polymer back bone providing capability for enhanced light absorption and excition dissociation[164]. Among the polythiophene derivatives, use of terthiophene (TTh) as precursor to the conducting polymer, poly (terthiophene) (PTTh) has been shown to yield photoelectrochemical cells (PECs) with enhanced photovoltaic (PV)
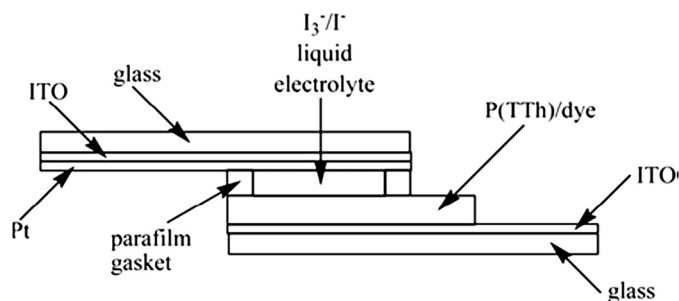

FIG. 3. Layout of photoelectrochemical cells (PECs) fabricated. Reprinted from Ref. [166]. Tsekouras, G.; Too, C.O.; Wallace, G.G. Photovoltaic properties of poly(terthiophene) doped with light harvesting dyes and photocurrent generation mechanism. Synt. Met. **2007**, *157*, 441–447.

performance compared to polythiophenes made from 3-methylthiophene (3MTh) or bithiophene (BTh)[165].

Tsekouras et al.[166] prepared (PEC) as illustrated in Figure 3, fabricated by placing a parafilm gasket containing a hole measuring $0.2 \times 0.2\,cm$ over (PTTh) /dye coated ITO glass electrode, followed by placing a drop of I_3^-/I^- liquid electrolyte over the hole in the gasket the Pt sputter-coated ITO coated glass counter electrode was then placed on top, ensuring no air bubbles entered into the I_3^-/I^- liquid electrolyte. The PEC was firmly held together using two alligator clips. Harris et al.[167] have fabricated a photo-electrochemical cell which is electrochemically deposited polyterthiophene films. In the study, the role of surface morphology in determining the photovoltaic characterisics of electrochemically deposited PTTh films was investigated. Sivakkumar et al.[168] have prepared a poly-(terthiophene) (PTTh)/multi-walled carbon nanotube (CNT) composite with in situ polymerization and used as an active cathode material in lithium cells assembled with an ionic liquid (IL) or conventional liquid electrolyte, $LiBF_4/EC$-DMC-DEC. The lithium cell assembled with a PTTh/CNT composite cathode and non-flammable IL electrolyte exhibited a mean discharge voltage of 3.8 V vs. Li^+/Li and is a promising candidate for high-voltage power sources with enhanced safety.

POLY(3-PHENYLTHIOPHENE)

The electrochemical behavior of the polymers of polythiophene series, PBT and P3PT, is studied in-situ. It is shown that in the case of the polymer of a more complicated composition than that of PBT, with additional possibilities for conjugation in the chain, additional absorption bands can be observed (490 and 550 nm for P3PT) as opposed to PBT, which is characterized by a single absorption band at 460–470 nm[169].

The p-nitrophenyl group is a redox active unit, which is of special interest for materials science and electrochemistry owing to its electro-catalytic properties[170], nonlinear

optical characteristics[171], biological activity[172] as well as the reproducibility of nitro group to amino group by both chemical and electrochemical approach[173]. The incorporation of such functional groups into conjugated π-electron systems such as polythiophenes[174] has been reported.

The interest in the electrochemistry and photo-electrochemistry of P3PT was also induced by the fact that the literature data on the possibility of cathodic doping of P3PT in the presence of alkali metal salts are controversial[175,176]. At the same time, this process is of great importance from the view point of employing P3PT in lithium batteries[177]. Guerrero et al.[178] have studied the relationship which is between the redox properties of a series of para-substituted 3-phenylthiophene monomers and obtained polymers with Hammett substituent constants, and found that there is a good relation between the redox properties and Hammett constants. Sato et al.[179] further demonstrated that the oxidation potential of P3PT increased when an electron-withdrawing substituent was placed on the phenyl ring and the electron-donating groups produced a stable anion-doped material. Thereby, the oxidation potential decreased[180]. A novel class of organic semiconducting materials, thiophene/phenylene-co-oligomers[181], 3-phenylthiophene, 2-phenylthiophene, 2,5-diphenylthiophene, 2-(2-thienyl)pyridine and 3,6-bis(2-thienyl) pyridazine under electrochemical and chemical conditions are reported in literature[182].

Poly(3-methoxythiophene)

Among the thiophene derivatives, poly(3-methoxythiophene) (PMOT) has drawn researchers' attention[183]. Because of its high solubility in the organic media, PMOT could not be directly electrodeposited as solid films on metalic substrates Fall et al.[184] showed that it is possible to obtain also PMOT in aqueous micellar solutions and specifically as electroactive conducting films on Pt[185,186] or iron. Fall and co-workers[187] have studied by EIS the PMOT-oxidized and neutral thin films in aqueous LiClO$_4$ solutions both the oxidized and neutral form of PMOT investigated PMOT films of different thickneses (0.25–0.75 µm) electrodeposited, impedance spectra were obtained at potentials ranging from 0 to 0.8 V/SCE. They showed the neutral form of PMOT behaves like an insulator.

Solar cells based on polymer material, such as poly(3-hexylthiophene) and poly(3-methoxythiophene),[188,189] and titanium dioxide could in principle offer production in high volume at low process cost. Research on the subject has focused mainly on improving the power conversion efficiency for small laboratory cells[190,191] through optimization of materials and the protocol used for preparation.

Han et al.[192] have reported solar cells based on hybrid of poly(3-methoxythiophene) and titanium dioxide nanocomposites. The method of preparing the titanium dioxide used supercritical fluid drying (SCFD) method, which was thought as an effective way to yield the nano-sized material and is widely used[193,194]. A series of conducting polymer complexes involving poly(3-methoxythiophene) with different quantities of titanium dioxide (PMOT/TiO$_2$) were synthesized by them. A solar-to-electric energy conversion efficiency of 0.35% was attained with the system.

Copolymerization of Thiophenes

In addition to functionalization of the thiophene ring, another concept extensively accepted to modify PT properties is the copolymerization process with different alkyl substituted thiophene. The formation a copolymer has been a common approach to materials with tailored properties. Earlier reports on chemically and electrochemically generated copolymers have appeared for thiophene and its alkyl derivatives. For example, copolymerization of thiophene with 3-methyl or 3-octylthiophene[195], as well as large number of copolymers based on 3-alkyl substituted derivatives, i.e., 3-methyl/3-octylthiophene[196], etc., but the solubility as a very important characteristic was still very limited.

Polythiophene films containing ester groups on the surface of electrodes are interesting potential carrier materials for reagents[197]. Methylthiophene-3-acetate can be copolymerized with 3-methylthiophene and 3-butylthiophene by means of cyclic voltammetry (CV) at potentials of 0–2.2 V. Higher potentials (0–2.4 V) lead to over-oxidation of the copolymers. Electrochemical investigations of 2,2'-bithiophene and at equimolar ratios showed no successful copolymerization at potentials of 0–1.3 V.

A random copolymer containing 3-methylthienyl methacrylate (MTM) and p-vinylbenzyloxy poly(ethyleneoxide) (PEO-VB) units was synthesized in literature[198]. Further graft copolymerization of CP with pyrrole (Py) and Th were achieved in H$_2$O-sodium dodecyl sulfate (SDS), H$_2$O-p-toluenesulphonic acid (PTSA) and acetonitrile (AN) – tetrabutylammonium tetrafluoro borate (TBAFB) solvent electrolyte couples via constant potential electrolyses. The synthesis of p-n conjugated copolymer, an alternating 3-dodecyloxythiophene, ethylene and pyridine backbone, were obtained by Heck Couple Method[199]. The electron donating and accepting groups on consecutive repeat units are introduced to stimulate intermolecular charge transfer along polymer chains.

The synthesized regioregular head to tail (HT) poly(3-dodecyl-oxythiophene) homopolymer via Grignard metathesis (GRIM)[200] method initially reported by McCullough et al. The newly synthesized poly(3-dodecyloxythiophene-2,4-vinylene) containing electron-donating thiophene unit and the electron-accepting pyridine unit, is expected to expand the scope of chemistry of POTs with such a charge-transferred (CT) structure. As a class of thiophene based copolymers, the fluorine-thieno [3,2-b]

thiophene-based conjugated copolymer poly(9, 9′-n-dioctyl-fluorene-alt-thieno [3,2-b]thiophene)[201]. Chujo et al.[202] have focused on the synthesis and properties of soluble donor-acceptor conjugated copolymers having a tricarbonyl (arene) chromium unit as an acceptor and a thiophene unit as a donor in the main chain.

The images reveal the coaxial structure of the resulting hybrid where the MWNT is encapsulated by a few-nanometer-thick layer of PProDOT. The surface of the tube appears to be grown well with increased thickness. There is a clear vicinity of MWNT core with a crystalline lattice structure and a fine layer around the tubes. Figure 4 represents the image of the copolymer hybrid, MWNT-g-PProDOT-co-PTh[203]. These images well correlate with the SEM results obtained, thus proving the grafting of PRoDOT onto the MWNTs.

The polymerization of methyl thiophene-3-acetate with 3-methyl thiophene and 3-butyl thiophene at potentials of $\Delta E = 0$–2.2 V under CV conditions gave in both cases copolymers containing ester groups. The covalently incorporated ester units of methyl thiophene-3-acetate can be proved by reflection IR spectra[204].

Levi et al[205]. have studied on the electrochemical activity of thin films of a conjugated copolymer, namely, poly(2,7-fluoren-9-one)-alt-(5,5′-(3,3′-di-n-octyl-2,2′-bithiophene)) (PFDOBT-HH; HH = head to head), synthesized electrochemically by a mild oxidation process at low current density. Using EIS, clear evidence is furnished for the presence of trapped, negatively charged species in the polymer bulk as a consequence of prolonged, consecutive n-doping.
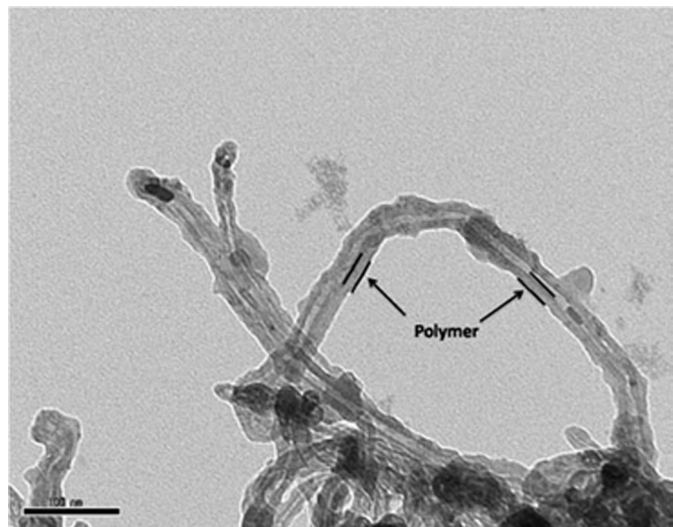

FIG. 4. Tunneling electron microscopy (TEM) image of MWNT-g-PProDOT-co-PTh. Reprinted from Ref. [203]. Kumar, N.A.; Kim, S.H.; Cho, B.G.; Lim, K.T.; Jeong, Y.T. Coll. Polym. Sci. **2009**, *287*, 97–102.

Xu et al. have prepared novel polyfluorene copolymers containing porphyrin and thiophene moieties via Suzuki coupling reactions[206]. These copolymers were soluble in common organic solvents. They were found to be thermally stable with initial decomposition temperatures over 398°C and together with high glass transition temperatures (117°C, ~152°C), to improve the operating lifetime of the solar cells. CV studies revealed that the band gaps of copolymers were between 1.96 and 2.03 eV.

CARBON MATERIALS

High performance carbon fibers can be obtained with thermoset and thermoplastic resin systems. Polyacrylonitrille (PAN) based carbon fibers are under continual development and are used in composites to produce materials of low density and greater strength. They are used for weaving, braiding and filament winding applications, unidirectional tapes and prepreg tow for fiber placement having excellent creep, fatigue resistance, high tensile strength and stiffness characteristics[207]. The application of a polymeric/co-polymeric "interface", acting as a coupling agent, can improve the interfacial properties between reinforcing carbon fibers and the polymeric matrix[208–210].

Modification of carbon fiber surfaces enhances the wetting properties of the surface and increases the possibility of forming attractive bonds (polar interactions, hydrogen and covalent bonds) between the reinforcing fibers and the surrounding matrix polymer. In order to obtain the optimal stress transfer, the formation of interfacial chemical bonds is desirable[211]. Modified reinforcing fibers have potential uses as advanced reinforced polymeric composite materials, to be used to form stronger structural materials for aircraft, spacecraft, and suspension bridges. Coated carbon fibers also have potential biosensor applications as microelectrodes working in small volumes of solutions. The disposable nature and low price of the carbon microfibers are advantages for their use as electrodes.

Carbon fibers (CF), which are a new breed of high-strength materials, are mainly used as reinforcements in composite materials such as CF-reinforced plastics, carbon-carbon composites, carbon fiber reinforced materials, and carbon fiber reinforced cement. Carbon fiber composites are ideally suited to applications where strength, stiffness, lower weight, and outstanding fatigue characteristics are critical requirements. They also find applications where high temperature, chemical inertness, and high damping are important in addition to having good electrical conductivity, thermal conductivity, and low linear coefficient of thermal expansion[212].

Conducting polymers have this potential due to their porous structure, but the electronic performance of polymer-based electrodes has yet to be fully developed[213,214]. Electropolymerization of pyrrole, carbazole, thiophene and their copolymers onto carbon fiber microelectrodes

(CFMEs) were investigated as a novel method for tailor-making CFME-polymer interphases to promote fiber matrix adhesion[215,216]. Electro-grafting of copolymer with conductive and nonconductive contents onto carbon fibers has recently been studied[217,218].

The possibility of high surface area electrodes with small dimensions has been realized in several applications: for example, for higher performance and miniaturization of electrochemical devices[219,220]. The electropolymerization of different monomers resulted in different polymers with distinctive properties, namely, conjugation length and, consequently, the intrinsic dc conductivity of the polymer was suggested by Roncali et al. as well[221]. On the other hand, the nature of the substrate on the surface potential of conducting polymer films affected the average value and the distribution of surface potential across the polymer surface[222].

Among the carbon electrodes, the carbon paste electrode (CPE) is of particular importance. The ease and speed of preparation and obtaining a new reproducible surface, the low residual current, porous surface and low cost of carbon paste are some advantages of CPEs over all other carbon electrodes. Therefore, the CPE can provide a suitable electrode substrate for preparation of modified electrodes[223]. Carbon-based nano-particles have been used in the metal ions analysis too. Mascaro and co-workers[224] succeed in fabricating a new electrode obtained by the dispersion of template carbon nanoparticles onto polyaniline. This new electrode exhibited good chemical and physical stabilities.

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

Electrochemical impedance spectroscopy (EIS) is an effective tool to validate the capacitance behavior. EIS has a well - developed theoretical background and established experimental procedures so that it serves as a convenient and readily available technique for obtaining important electrochemical information, such as electrolyte resistance, charge transfer resistance, and Faradaic capacitance[225–227]. EIS was carried out to prove the capacitive performance in the frequency range of 0.01 Hz to 100 kHz with AC-voltage amplitude of 10 mV. EIS is powerful technique to describe the surface configuration of the electrode[228]. Nyquist plots were the most frequently used figures to indicate the electrochemistry response, Nyquist plots were also obtained, from which the information about the double layer was hardly acquired[229].

A combination of EIS with standard electrochemical methods such as CV, provides a powerful tool to understand the properties of conducting polymer and thus to develop useful compounds for the specific applications[230]. Studies on nano-composites and electrochemical nano-and micron sized capacitor are very attractive due to their higher energy densities through the small volume of material[231]. There is another important factor: the variation of the electrolyte concentration in the interphases (but outside the double layer) influencing both the overall accumulated interfacial parameters must also be present in the overall impedance[232]. Electric double layer capacitor (EDLC) forms on carbon as the electrodes and stores charge in the electric field at the interface which can be either aqueous or non-aqueous electrolyte. It gives high power density but low energy density[233].

Abe and co-workers[234] have prepared highly oriented pyrolytic graphite (HOPG) and graphitized carbonaceous thin films by plasma-assisted chemical vapor deposition (PACVD), surface modified by electropolymerization of thiophene. The electrochemical properties of the carbonaceous materials were studied by cyclic voltammetry and AC impedance spectroscopy. On the Nyquist plots, a semi-circle due to surface film resistance was observed, and the value significantly decreased at around 1.5 V. At potentials below 0.9 V, another semi-circle appeared in the middle to lower frequency region, assigned to the charge transfer resistance due to lithium ion transfer at the surface-modified carbon electrode/electrolyte interface.

Nyquist plots the surface modified carbonaceous film was treated at 4.8 V for 10 s as shown in Figure 5a. Electrode potentials were ranging 2.0–0.8 V. At a potential of 2.0 V, only one semi-circle appeared in the higher frequency region. The resultant carbonaceous thin film electrode shows an electric conductivity of greater than $100 \, S \, cm^{-1}$, and hence this semi-circle is not due to electrical resistance of the electrode. Based on the results of the CV, no lithium ion insertion or extraction occurs at this potential, and therefore the semi-circle in the higher frequency region is derived from the surface film on the electrode.

When the potential decreased to 1.2 V, the surface film resistance dramatically decreased and gave a small semi-circle with a characteristic frequency of 400 Hz. As mentioned above, this feature seems to be associated with doping of lithium-ion into the electro-conductive surface film. At a potential of 0.8 V, another semi-circle appeared in the lower frequency region. From the voltammograms, lithium-ion was inserted into the electrode potantials. Therefore, it is likely that the resistances can be ascribed to the charge (lithium-ion) transfer resistances. Nyquist plots for a surface modified carbonaceous thin film electrode at potentials of 0.6–0.02 V was shown in Figure 5b.

As is clear from this figure, semi-circles due to the surface film and charge transfer resistances are completely overlapped and apparently only one semi-circle is observed. By deconvolution of the Nyquist plot at a potential of 0.8 V, the semi-circle due to surface film resistance gives a resistance of ca. 250 Ω. Moreover, the minimum value of total resistance was as low as 280 Ω at lower potentials of 0.02 V, and therefore the value of the charge transfer resistance was evaluated to be around 30 Ω. These
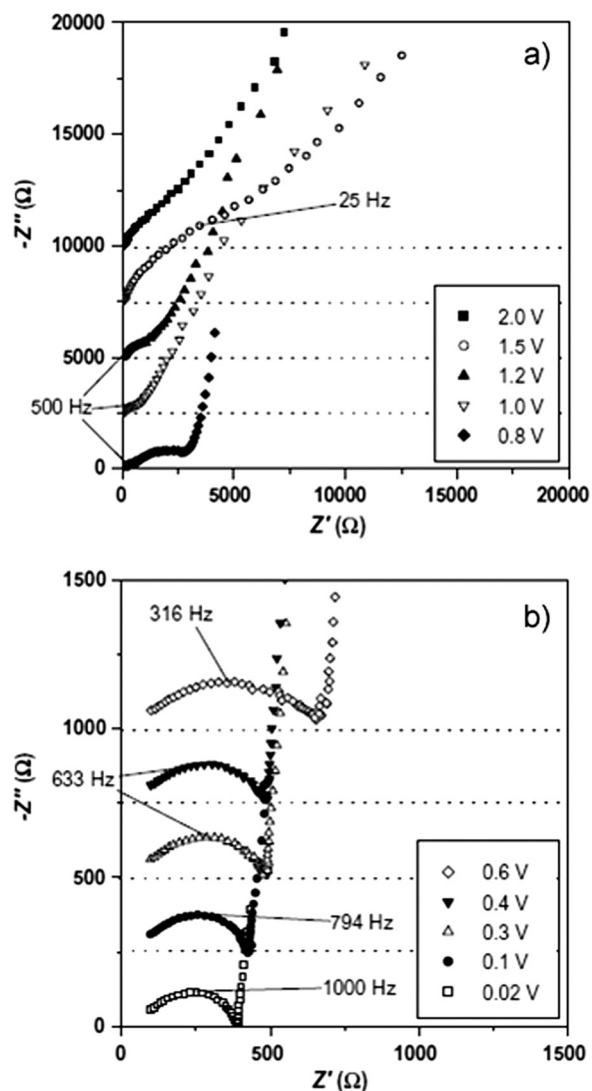
FIG. 5.   Impedance spectra of a carbonaceous thin film treated at 4.8 V for 10 s in 1 mol.dm^{-3} LiClO$_4$ + 12.7 mmol · dm^{-3} thiophene/PC. Electrolyte solution was 1 mol · dm^{-3} LiClO$_4$/EC + DEC. a) Electrode potential was kept at 2.0, 1.5, 1.2, 1.0 and 0.8 V. b) Electrode potential was kept at 0.6, 0.4, 0.3, 0.1 and 0.02 V. Reprinted from Ref. [236]. Doi, T.; Takeda, K.; Fukutsuka, T.; Iriyama, Y.; Abe, T.; Ogumi, Z. Carbon 2005, 43, 2352–2357.

values were quite identical to those obtained for the untreated carbonaceous thin film[235]. From these results, surface film can be effectively formed on the surface-modified carbonaceous thin films with irreversible current suppressed[236].

Levi et al.[237] have studied CV characterizations of poly-3-(3,4,5-trifluorophenyl) thiophene (PTFPT) film electrodes in contact with acetonitrile (AN), propylene carbonate (PC) and tetra methylene sulfone (TMS) showed a pronounced, solvent-dependent slow-down of the p- and n-doping/undoping kinetics in the sequence AN > PC > SF. Further characterization using EIS revealed two specific

features: (i) in the high frequency region, Nyquist plots for n-doping in the TEABF$_4$/sulfolane (SF) solution, were drastically different from these for PC and AN solutions, ascribed to the low bulk conductivity of the doped film in the SF solution; (ii) in the low frequency region, Nyquist plots for n-doping in an AN solution, showed a distinct semicircle with a relatively high resistance, in contrast to a well-known, sloping capacitive line, typical of a low-frequency behavior of the same film in contact with PC and SF solutions.

EIS involves measuring the electrode impedance over a spectrum of frequencies. Not only can it determine the magnitude of the resistive and capacitive response, but it can also examine their performance over a wide range of frequencies. Xiao et al.[238] have studied the impedance, measured over a range of frequencies from 10^0 to 10^5 Hz. Magnitude and phase information, which characterizes the impedance, was measured directly. By using these data, one can obtain qualitative and quantitative information about the electrical properties of the coated and uncoated electrodes. One kilohertz is the frequency characteristic of neutral biologic activity; therefore, impedance at this point is frequently used as a standard to evaluate a neuralelectrode[239].

It is concluded that the nature of supporting electrolyte anions and solvent insignificantly affect the form of electrochemical responses of poly(3,4-ethylenedioxythiophene) films[240]. The main contribution into the stabilization of positively charged redox fragments that appear in the polymer chain of PEDOT is probably determined by the electron-donating properties of the oxygen atoms in the substituent.

Supercapacitors

The demand for clean energy is rapidly expanding worldwide and one of the most promising solutions proposed is non-polluting energy production by fuel-cells[241]. Supercapacitors or electrochemical capacitors (EC) are energy and power storage devices that have technical and economical advances in a diverse range of consumer and industrial applications, including electrical vehicles, uninterruptible power supplies, and memory protection of computer electronics, cellular communication devices and fuel cells or batteries[242], which supercapacitors use for energy storage due to their capability to deliver high specific power during a few seconds or more, are presently considered as the electrical energy storage devices[243].

Supercapacitors can be used in numerous applications, also in electric or hybrid vehicles in order to provide peak power for improved acceleration, for energy recovery, in parallel with the vehicle battery during start-up of a thermal engine with the purpose of decreasing the size and the power of the battery, in fuel cell vehicles in order to reduce the power, and therefore, the cost of the fuel cell[244].

Supercapacitors fill the gap between batteries and conventional capacitors in terms of their specific energy and

specific power. A supercapacitor is a very similar to batteries except that: i) the electrodes used are usually identical and ii) the charge storage in electroactive electrode materials is capacitive in origin involves mainly the translational motion of charged species[245]. Two type of electrochemical capacitor are currently under development, namely, the electric double-layer capacitor (EDLC) and redox-or pseudo-capacitor (PsC)[246]. In the former, energy storage arises mainly from the separation of electronic and ionic charges at the interface between electrode materials with a high specific area and the electrolytic solutions. In the latter, fast faradic reactions occur in the electrode materials at characteristic potentials.

Supercapacitors have attracted much attention because of their higher power density, better efficiency, and longer durability in comparison to the rechargeable batteries[247]. Commercial devices are mainly based on two symmetric activated carbon electrodes and organic electrolyte, which has higher voltage stability than water medium. However, devices with organic electrolytes are ecologically unfriendly, less safe, and more expensive because of specific preparation conditions.

Moreover, organic electrolytes have electrical conductivity two orders of magnitude smaller than the aqueous medium; hence, it reduces available power, which is another series drawback. It can be seen that using an aqueous electrolyte would be more interesting from an industrial point of view; but in an aqueous solution, despite of high specific devices is limited to 1 V, and subsequently, both power and energy densities remain unsatisfactory for industrial applications[248].

The oxidation and reduction (redox) processes in ECP make it possible to use these polymer materials as charge storage devices, either as battery electrodes or as supercapacitors. The potential for reduced cost, weight, and environmental impact of ECP electrodes relative to the metals and metal oxides that are traditionally used in such devices makes these polymers attractive alternatives[249]. Conjugated polymeric systems offer several advantages such as high charge density, fast charge-discharge processes, adequacy of morphology, and low cost. Conductive polymers have also been used in electrode material of supercapacitor for fabrication of composite electrodes with other polymeric[250,251] and carbon-based materials[252–255].

Zhang et al.[256] have studied PPy/activated carbon (AC) composite electrodes, which is its specific capacitance is 345 F/g at 0.9 V working voltage. Using AC as substrate material is being expected as a way to relieve the instabilities because that adhesion and charge transfer conductivities between the PPy and substrate can be improved. Li et al. have studied a poly(2,2,6,6-teramethylpiperidinyloxy methacrylate) nitroxide polyradical AC is used as the negative electrode material. The capacity of the composite electrode is 30% larger than that of the pure AC electrode[257].

Park et al.[258] have prepared a composite electrode, via chemical polymerization of pyrrole on the surface of a porous graphite fiber matrix, for super capacitor. The electrode's specific capacitance was about 400 F/g and Coulombic efficiency was 96–99%. PEDOT[259,260], a derivative of PTh, is an interesting material in view of its good thermal and chemical stability, fast electrochemical switching, and a high electrical conductivity in the –doped state (easily up to $550\,S\,cm^{-1}$)[261].

However, the specific capacitance of PEDOT was smaller than that of PPy, due to monomer unit (3,4-ethylene-dioxythiophene, EDOT) with the greater molecular weight than pyrrole. To over come this drawback, Wang et al.[262] have prepared with galvanostatic polymerization of PEDOT on the PPy modified electrode. PEDOT/PPy composite electrodes had greater specific capacitance than that of pure PEDOT electrodes. They reported PEDOT/PPy composite (5:1) electrodes showed a specific capacitance of 290 F/g and good cycling performance in 1 M KCl solution. A symmetric redox supercapacitor has been fabricated based on n and p doped PEDOT coated on stainless steel (SS) electrodes by Bhat et al.[263]. The supercapacitor showed a maximum specific capacitance of $121\,F\,g^{-1}$ at a scan rate of $10\,mV\,s^{-1}$. The time constant calculated for the supercapacitor through the active-reactive power behavior measurement was 12 milliseconds indicating the suitability of the system for efficient use at low frequency range. Capacitance enhancement of the ECs through introduction of functional groups or materials possessing redox properties has been investigated in literature[264,265].

There has been intense interest in nanotubes (CNTs), since their discovery by Lijima in 1991[266] due to their unique properties, such as high electrical conductivity, high chemical stability, extremely high mechanical strength, have a novel structure, a narrow distribution size, highly accessible surface area, low resistivity, and high stability[267]. Carbon nanotubes behave electrically either as metals or semiconductors depending on their atomic structure[268], and have been used as electrode materials[269]. A subtle electronic property suggests that carbon nanotubes have the ability to promote electron-transfer reaction when used as an electrode material. But, fabrication and application of carbon nanotubes by using a piece of carbon nanotube electrode is difficult due to the diameter very small (5–50 nm)[270].

Several attempts are being made to use carbon nanotubes for the double-layer supercapacitors[271–273]; however, the values of capacitance are lower than those of the best activated carbon[274]. On the other hand, due to the versatility of structure and low cost compared with noble metal oxides, electronically conducting polymers (ECPs) represent a promising class of active materials for electrodes of the redox supercapacitors. In the doping process, charging

takes place throughout the volume of ECPs. The modification of carbon nanotubes by ECPs is a feasible way to enhance capacitance[275,276].

It has been shown CNTs play the role of a perfect backbone for a homogeneous distribution of ECP active material from mechanical changes (shrinkage and breaking) during long cycling. Apart of excellent conducting and mechanical properties, the presence of nanotubes improves also the charge transfer that enables a high charge/discharge rate. For an optimal use of ECPs in electrochemical capacitors, a special electrode composition with ca. 20 wt% of CNTs and a careful selection of the potential range is necessary. Frackowiak et al.[277] tested ECP, polyaniline (PANI), polypyrrole (PPy) and poly-(3,4-ethylenedioxythiophene) (PEDOT), as supercapacitor electrode materials in the form of composites with multiwalled carbon nanotubes (CNTs). They reported the specific capacitance values ranging from 100 to 330 F/g could be reached for different asymmetric configurations with capacitor voltage from 0.6 to 1.8 V.

Circuit Modeling

Several circuits were tested to fit the EIS spectra of PBT, including these found in the literature for other polythiophene derivatives[278], but were unsatisfactory (poor χ^2 correlation coefficients). However, Fall et al.[279] obtained good fittings for frequencies ranging from 0.1 to 10.000 Hz ($\chi^2 \cong 10^{-5} - 10^{-4}$) by using the equivalent circuit depicted in Figure 6. The EIS spectra of PBT films were analyzed using the model (QR)((CR)(QR)). The circuit is similar to that of PMOT film impedance spectra, but the first pure capacitance observed in the case of PMOT is replaced by a constant phase element with exponents close to 1. No solution resistance was found in the prospected domain, as for PMOT[280].

Andrieux et al.[281] have studied the constant electron transfer between the metallic substrate and the conducting polymer film. Moreover, the rate determining step for the charge transport is the transition of the electron from one

redox side to a neighboring one. This transition is also known as an "electron hopping" process that has diffusion nature. The charge diffusion coefficients, Dc, are of the order of 10^{-10}–10^{-13} cm^2 s^{-1}. A "Warburg" type diffusion impedance element is normally used to describe this charge-hopping process[282]. The rate-determining step in the case of poly(alkylthiophene) is the electron movement from one polymer chain to another[283]. The kinetics of charge transfer in PMT/sol-gel (MPc) film is therefore similar to a redox polymer, but with relatively high ionic and low electronic conductivities. It might be important at this stage to separate the double layer charging of the metal-film interface from the interfacial oxidation-reduction of the polymer and the associated diffusion-type electron transport across the film. When the hybrid film is oxidized, its electronic conductivity will exceed that of the mobile counter ions within the film matrix[284].

Therefore, when an electrical field is established within the film, ions migrate to reach equilibrium. The film behaves in this case a porous metal with pores of limited depth and size. According to De Levie[285], the impedance of a one dimensional cylindrical pore structure with invariant interfacial impedance, Z_o, along the wall of the pores can be described by a transfer function. It is possible to correlate the data to "modified" Randles circuits that are shown in Figures 7a, 7b. In the following set of equations, the terms are described as follows: Z_p, $R_{\Omega,p}$, $Z_{\omega,p}$, r_p and I_p are the impedance of a single pore, the electrolytic resistance, the impedance of the pore wall in the polymer film, the radius of the pore wall in the polymer film, the radius of pore, and the length of pore, respectively.

$$Z_p = \sqrt{R_{\Omega,p} . Z_{\omega,p}} \coth \sqrt{R_{\Omega,p}/Z_{\omega,p}} \quad (1)$$

$$R_{\Omega,p} = I_p/\sigma . \pi . r_p . I_p \quad (2)$$

$$Z_{\omega,p} = Z_o/2 . \pi . r_p . I_p \quad (3)$$

The Warburg element, w (with a corresponding impedance of Z), in Figure 7 represents a linear finite restricted diffusion of some species throughout the film, namely, anionic dopants. In the low frequency region, the finite-length Warburg diffusion element (Z_D) is characterized by a diffusion time constant (τ_D), a diffusion pseudo-capacitance (C_D), and a diffusion resistance (R_D) that can be related by the following expressions[286]:

$$Z_D = (\tau_D/C_D) \coth(j . C_{TD})^{1/2}/(j_\omega . C_D)^{1/2} \quad (4)$$

Several electrical circuits were initially tested by nonlinear least-squares fitting of the experimental impedance data. The equivalent circuit was found to give excellent fits down to frequencies including the low frequency corresponding
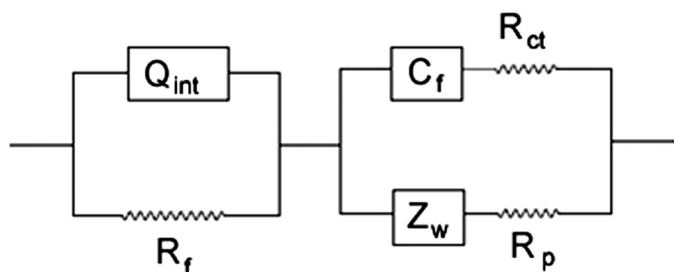
FIG. 6. Equivalent electrical circuit for Pt/PBT electrodes. Reprinted from Ref. [279]. Diagne, A.A.; Fall, M.; Guene, M.; Dieng, M.M.; Deflorian, F.; Rossi, S.; Bonora, P.; Volpe, C.D. C.R. Chimie 2007, 10, 558–563.
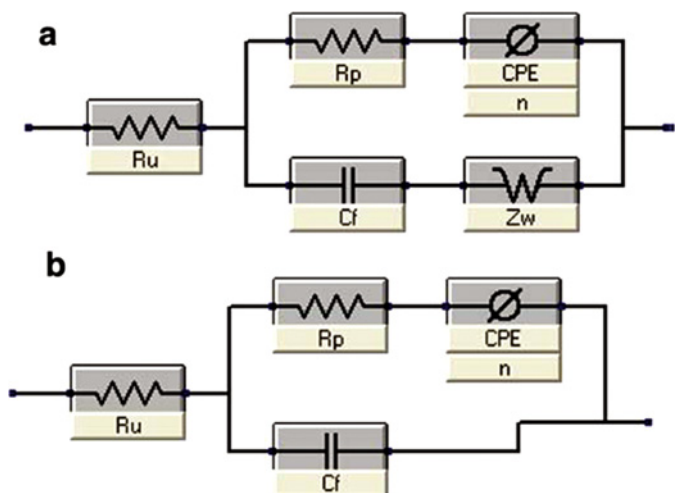
FIG. 7. Equivalent circuits used in the fit procedure of the impedance spectrums. The results were analyzed using Levenberg-Marquardt/ Simplex algorithms based on a complex non-linear least-squares procedure. Reprinted from Ref. [76]. Galal, A.; Darwish, S.A.; Ahmed, R.A. J. Solid State Electrochem. **2007**, *11*, 531–542. (Color figure available online.)

FIG. 9. Electrical equivalent circuit used for simulating the experimental impedance data from 0.2 to 1.2. V. Reprinted from Ref. [290]. Cebeci, F.Ç.; Sezer, E.; Sarac, A.S. Electrochim. Acta **2009**, *54*, 6354–6360. (Color figure available online.)

to the bulk capacitance (at low frequency) of the polymer film (Fig. 7). Bobacka et al.[281] showed considerable deviation from capacitive lines at low frequencies. The model is composed of the solution resistance (Ru), the double layer capacitance (CPE), the low-frequency bulk-redox capacitance (C_F), and the "classical" semi-finite Warburg diffusion element (Z_D). The finite-length Warburg diffusion element Z_D is characterized by the diffusional time constant (a_D), the diffusional pseudo-capacitance (C_D), and the diffusion resistance (R_D) only in the low-frequency region.

The effect of thermal annealing of poly(3-octylthiophene) (P3OT) coatings on the corrosion inhibition of stainless steel in an NaCl solution was investigated[287]. Equivalent electric circuits to simulate EIS data for

uncoated and P3OT-coated 304SS are given in Figure 8. CPE_{coat} and R_{coat} represent the capacitance and resistance of the coating, respectively. CPE_{dl} represent the constant phase element of the electrochemical double layer, and W represent impedance Warburg.

Levi et al.[288] observed that Nyquist plots for thin layer graphite electrode were typically characterized by a sloping at low-frequency, stated to deviate from the classical Warburg line at relatively high frequencies[289]. This behavior was explained by a unique, serial combination of finite-space and finite-length elements for a composite graphite electrode composed of platelet, highly oriented particles.

Cebeci et al.[290] have used in simulation of impedance behavior of poly(3,4-ethylenedioxythiophene)-(4,4′-dinonyl-2,2′-bithiazole) film from the experimentally obtained impedance data (Fig. 9) for an electric equivalent circuit. The proposed model (Fig. 9) was used in the electro-active region (i.e., 0.2–1.2 V) of the electrode. This model was built using series components; the first one is the solution resistance of the polymer electrode and the electrolyte, Rs, second one the parallel combination of the double layer capacitance, C_{dl}, and R_1 is the charge transfer resistance between polymer electrode and electrolyte interface.

The series combination to R_1 made up using constant phase element (CPE) in parallel with R_2 and W, R_2 is the resistance of the polymer film, and W is the Warburg impedance of diffusion of the ions in the electrolyte. The last component a capacitor element (C_{CF}) is introduced in parallel with a charge transfer resistor (R_{CF}) corresponding to the carbon fiber microelectrode is equivalent to the charge transfer from the polymer coating to the carbon fiber.
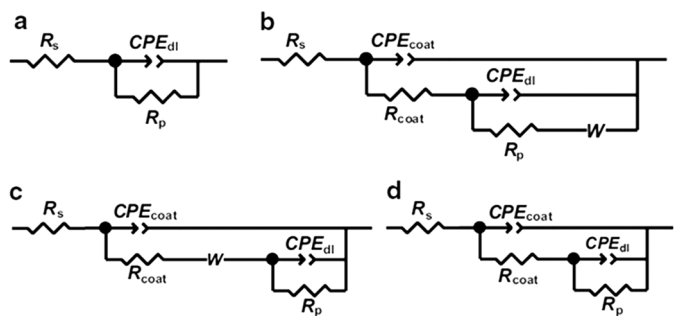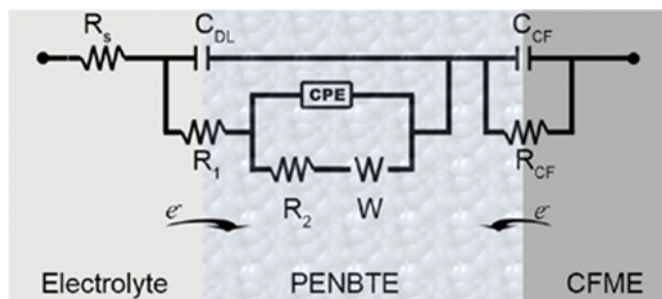

FIG. 8. Equivalent electric circuits used to simulate electrochemical impedance spectroscopy data for a) uncoated 304SS and P3OT-coated 304SS annealed at b) 55°C, c) 80°C and d) 100°C. Reprinted from Ref. [287]. Leon-Silva, U.; Nicho, M.E.; Gonzalez-Rodriquez, J.G.; Chacon-Nava, J.G.; Salinas-Bravo, V.M. J. Solid State Electrochem. **2010**, *14*, 1089–1100.

CONCLUDING REMARKS

Substituted polythiophenes have been examined on carbon materials, as well as polythiophene derivatives and their copolymers are investigated in this review. Carbon materials, especially carbon nanotubes have highly

increased the capacitive behaviour. A few polymers, like PEDOT, are used as supercapacitor electrode materials. Many different circuit modeling evaluations for polythiophenes which have been reported in literature are presented.

ABBREVIATIONS

Acid oxidation: (AO); Acetonitrile: (AN); Charge transfer resistance: (R1); Constant phase element: (CPE); Charge-transfer: (CT); Carbon fiber microelectrode: (CFME); Conducting polymers: (CPs); Carbon nanotubes: (CNTs); Copper phthalocyanine: (CuPc); Carbon fiber: (CF); Cyclic voltammetry: (CV); Chemically polymerized: (CP); Carbon paste electrode: (CarPE); Double layer capacitance: (C_{dl}); Electronic double layer capacitance: (EDLC); Electrochemical capacitors: (EC); Electrochemical impedance spectroscopy: (EIS); Electronically conducting polymers: (ECPs); 3,4-ethylenedioxythiophene: (EDOT); Ethyl 2-amino 4,5,6,7-tetrahydrobenzo thiophene-3-carboxylate maleimide: (ETTCM); Feet-effect transistors: (FETs); Fourier Transform Infrared Spectroscopy- Attenuated Total Reflectance: (FTIR-ATR); Glassy carbon: (GC); Grignard metathesis: (GRIM); Highly oriented pyrolytic graphite: (HOPG); Head to tail: (HT); Hydrodesulphurization: (HDS); Inorganic oxide: (WO_3); Ion-selective electrodes: (ISEs); Impedance spectroscopy: (IS); Liquid-crystalline: (LC); Lithium perchlorate: ($LiClO_4$); Multi walled carbon nanotubes: (MWNTs); 3-methylthienyl methacrylate: (MTM); Poly(2,7-fluoren-9-one)-alt-(5,5′-(3,3′-di-n-octyl-2,2′-bithiophene): (PFDOBT-HH); poly-3-(3,4,5-trifluorophenyl) thiophene: (PTFPT); Polythiophene: (PT); Poly(methylthiophene): (PMT); Poly(3-methylthiophene): (P3MT); Polyvinylidene fluoride: (PVDF); Polypyrrole: (PPy); Poly(3-hexylthiophene): (P3HT); Poly(3,4-ethylenedioxythiophene): (PEDOT); Poly(3′,3′-diheptyl-3,4-propylenedioxythiophene): poly (hepthyl$_2$-PDOT); Poly(3,4-propylenedioxythiophene): (PPoDOT); 3,4-propylenedioxythiophene: (ProDOT-OH); p-vinylbenzyloxy poly(ethyleneoxide): (PEO-VB); p-toluenesulfonic acid: (PTSA); Polyacrylonitrile: (PAN); Plasma-assisted chemical vapor deposition: (PACVD); Propylene carbonate: (PC); Polybithiophene: (PBT); Poly(4,4′-bis(alkylsulfonyl)-2,2′-bithiophene]s: (PRST); Perhydrotriphenylenylene: (PHTP); Poly(octylthiophene): (POT); Pseudo-capacitor: (PsC); Poly(3-dodecythiophene): (PDDT); Poly(terthiophene): (PTTh); Supercapacitors: (SCP); Stainless steel: (SS); Sodium dodecyl sulfate: (SDS); Scanning electron microscopy: (SEM); Tetrabutyl ammonium perchlorate: ($TBAClO_4$); Tetrabutylammonium tetrafluoroborate: (TBAFB); Tunneling electron microscopy: (TEM); Tetrabutyl ammonium hexafluorophosphate: ($TBAPF_6$); Tetraethylammonium perchlorate: ($TEAClO_4$); Tetra methylene sulfone: (TMS); Vapour phase polymerization: (VPP);

X-ray diffraction spectroscopy: (XRD); X-ray photoelectron spectroscopy: (XPS).

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