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Filmy na bázi vodivých polymerů pro přeměnu a skladování energie
Conducting polymers-based films for energy conversion and storage

Disertační práce

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Doctoral thesis

Supervisor: **Ing. Patrycja Bober, Ph.D.**

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List of abbreviations and notations

CPs	Conducting polymers
PPy	Polypyrrole
PA	Polyacetylene
PANI	Polyaniline
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
ACN	Acetonitrile
Me₄NCF₃SO₃	Tetramethylammonium trifluoromethanesulfonate
PbO_x	Lead oxide
TBABF₄	Tetrabutylammonium tetrafluoroborate
MnO_x	Manganese oxide
V_xO_x	Vanadium oxide
HBF₄	Fluoroboric acid
CNT	Carbon nanotube
PC	Propylene carbonate
CoN₄	Cobalt complex
TBAPF₆	Tetrabutylammonium hexafluorophosphate
ddH₂O	Deionized water
GrO	Graphene oxide
CNXL	Cellulose nanocrystal
MOF	Metal organic framework
EGN	Graphite nanosheet
MB	Magnetic biochar

AC	Activated carbon
NT or NTs	Nanotube or nanotubes
rGO	Reduced graphene oxide
FEG	Functionalized partial-exfoliated graphite
PrGO	Polypyrrole-reduced graphene oxide matrix
ECNT	Electrochemically pretreated CNT
SEM	Scanning electron microscopy
XRD	X-ray diffraction spectroscopy
UV-Vis	Ultraviolet-visible spectroscopy
CV	Cyclic voltammetry
GCD	Galvanostatic charge-discharge
EIS	Electrochemical impedance spectroscopy
AB25	Acid Blue 25
AB129	Acid Blue 129
MO	Methyl orange

Declaration:

This thesis presents my original work and is not substantially the same as any work that has been or is being submitted to any other University for any degree, diploma, or any other qualification.

Prague, 24 October 2024

Doebner Von Tumacder

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Conducting polymers-based films for energy conversion and storage

ABSTRACT

Polypyrrole (PPy) is one of the most promising conducting polymers owing to its excellent conductivity, redox properties, and stability. The aim to develop PPy nanostructures is to significantly improve PPy's conductivity and electroactivity relevant for high performance supercapacitors. Recently, the addition of organic dyes to the polymerization of pyrrole has noticeable influence on the morphology, conductivity, and electrochemical stability of PPy. The presence of organic dyes during the chemical and electrochemical polymerization of PPy has the ability to modify the typical globular morphology of PPy to nanotubes or nanofibers with enhanced conductivity. In this study, the electrochemical properties of chemically and electrochemically prepared PPy in the presence of Safranin-O, Acid Blue 25, Acid Blue 129 and methyl orange were investigated. Specifically, electroactivity, capacitance, stability, and morphology of the obtained films were elucidated through various characterization techniques (i.e. cyclic voltammetry, galvanostatic charge-discharge, electrochemical impedance spectroscopy, and scanning electron microscopy). Results showed that the presence of organic dyes during the electrochemical polymerization of PPy has shown a significant increase in the electroactivity of PPy with an enhanced electrochemical capacitance. An improved electrochemical stability was observed in the presence of organic dyes wherein only minimal changes in the electrochemical capacitance was observed during long potential cycling. The excellent electrochemical performance is ascribed to the nanostructured morphological network of PPy, giving rise to the increased electrolyte-accessible active areas. In addition, a PPy-based supercapacitor device was assembled based on the chemically prepared nanostructured PPy in order to demonstrate its energy storage characteristics. The device showed good capacitive behavior and stability with excellent energy and power density. These positive results serve as an indication that modifying the morphology of PPy can be the groundwork to fulfill the demands of a high performing supercapacitor as an energy storage device.

Keywords: Conducting polymers, Polypyrrole, Organic dyes, Supercapacitors, Energy storage devices

Filmy na bázi vodivých polymerů pro přeměnu a skladování energie

ABSTRAKT

Polypyrrol (PPy) je jedním z nejslibnějších vodivých polymerů díky své vynikající vodivosti, redoxním vlastnostem a stabilitě. Cílem vývoje nanostruktur PPy je výrazně zlepšit vodivost a elektroaktivitu PPy, což je důležité pro vysoce výkonné superkondenzátory. V poslední době má přidavek organických barviv k polymeraci pyrrolu znatelný vliv na morfologii, vodivost a elektrochemickou stabilitu PPy. Přítomnost organických barviv během chemické a elektrochemické polymerace PPy má schopnost modifikovat typický kulovitý PPy na nanotrubičky nebo nanovlákná se zvýšenou vodivostí. V této studii byly zkoumány elektrochemické vlastnosti chemicky a elektrochemicky připravených PPy v přítomnosti Safranin-O, Acid Blue 25, Acid Blue 129 a methylové oranžové. Konkrétně byla objasněna elektroaktivita, kapacita, stabilita a morfologie získaných filmů pomocí různých charakterizačních technik (tj. cyklické voltametrie, galvanostatického náboje a výboje, elektrochemické impedanční spektroskopie a skenovací elektronové mikroskopie). Výsledky ukázaly, že přítomnost organických barviv během elektrochemické polymerace PPy ukázala výrazné zvýšení elektroaktivity PPy se zvýšenou elektrochemickou kapacitou. V přítomnosti organických barviv byla pozorována zlepšená elektrochemická stabilita, kdy během dlouhých potenciálových cyklů byly pozorovány pouze minimální změny elektrochemické kapacity. Vynikající elektrochemické vlastnosti jsou přisuzovány nanostrukturní morfologické síti PPy, která vede ke zvýšení aktivních ploch přístupných elektrolytu. Kromě toho bylo na základě chemicky připraveného nanostrukturovaného PPy sestaveno superkondenzátorové zařízení s cílem prokázat jeho vlastnosti při skladování energie. Zařízení vykazovalo dobré kapacitní chování a stabilitu s vynikající hustotou energie a výkonu. Tyto pozitivní výsledky slouží jako náznak toho, že modifikace morfologie PPy může být základem pro splnění požadavků na vysoce výkonný superkondenzátor jako zařízení pro ukládání energie.

Keywords: Vodivé polymery, Polypyrrol, Organická barviva, Superkondenzátory, Zařízení pro ukládání energie

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Chapter 1 Introduction

1.1 Conducting polymers

Conducting polymers (CPs) are a special class of materials since MacDiarmid et al. discovered in 1977 the conducting properties of polyacetylene (PA) [1]. CPs has evolved dramatically through these years wherein they demonstrate remarkable optical and electrical properties. Typical examples of CPs are polyacetylene (PA) [2], polyaniline (PANI) [3], polypyrrole (PPy) [4], polythiophene [5], etc. (see Figure 1). The characteristic feature for these polymers is the delocalized π – electron system consisting of alternating single and double bonds or linked aromatic rings along their backbone [6], [7], [8]. For CPs to become conducting, they must contain overlapping π – molecular orbitals (p_z orbitals) and a high degree of π – bond conjugation. These conjugate bonds are the reason for the electrons to move around the polymer backbone and responsible for its conducting property.

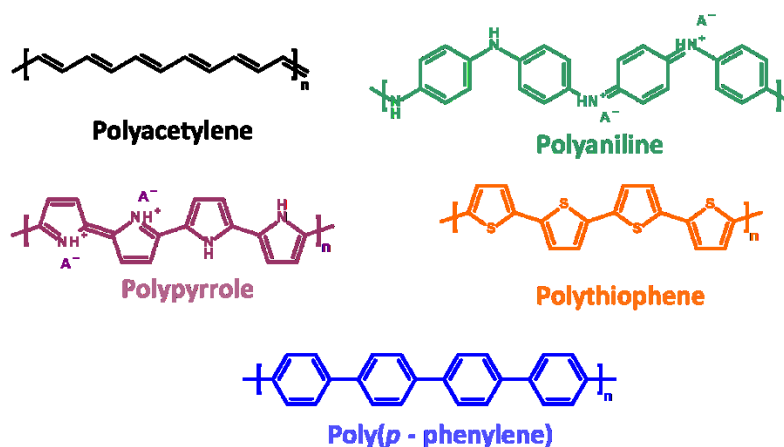


Figure 1. Examples of some typical conducting polymers.

Also, the conductivity of CPs depends on the dopant material. By means of doping, the polymer undergoes redox reactions wherein electrons are being added or withdrawn in or from the polymer backbone [9]. Two types of doping are being identified: (1) *p* – type doping and (2) *n* – type doping in which positive and negative polarons/bipolarons (known as charge carriers) are created [10]. Polarons/bipolarons are delocalized all over the polymer chain which aids to the electronic conductivity of CPs [11]. For *p* – type

doping, the electrons move from HOMO (or the host HOMO) to the dopant species creating a hole in the polymer backbone making it to be electron deficient (see Figure 2) [12], [13]. In particular, when a π – bond electron is removed from the polymer backbone, a radical cation defect (called polaron) is formed, thereby making the polymer conducting. Upon its removal, the remaining electrons in the π – orbital become delocalized along the conjugated polymer backbone making the polymer to freely move along its chain. The formed positive charged polymer backbone is then accompanied by a dopant anion in order to electrostatically balances the positive charges. The n – type doping (shown in Figure 2), on the other hand, is the opposite of p – type doping where the electrons moves towards the LUMO (or host LUMO) and an increase in the electron density on the polymer chain is observed [12], [13]. These electrons increase the electron conductivity of the polymer.

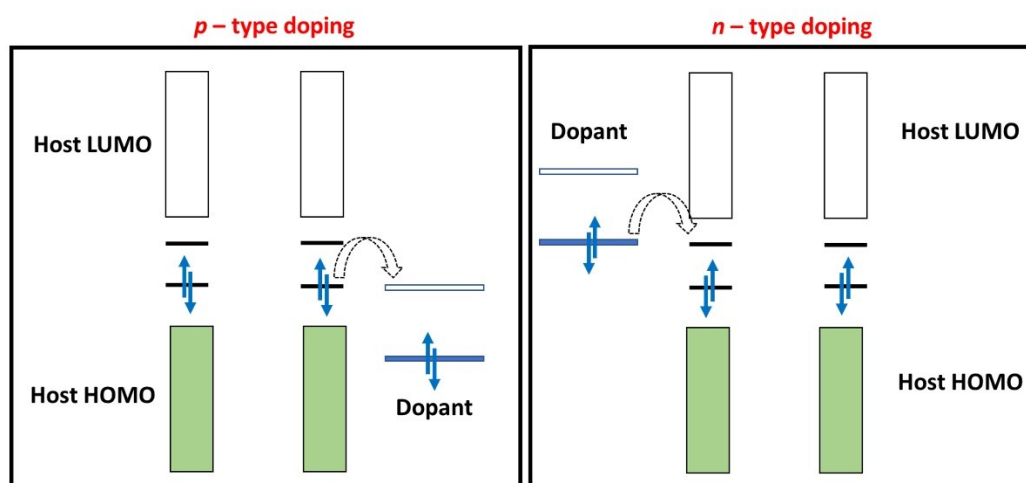


Figure 2. Schematic representation of p – type and n – type doping mechanism.

Moreover, because of doping, CPs can particularly behave as insulators, semiconductors, or conductors depending on their doping level as shown in Figure 3. Aside from its unique optical and electrical properties, CPs have low density and high environmental stability similar to other polymers. Conducting polymers can be easily prepared at low cost as well. In particular, one of the advantageous attributes CPs possess is its controllable optical, electrical, chemical, and/or mechanical properties. Due to this array of substantial

properties, CPs are used in a variety of applications such as in mechanical actuators [14], [15], [16], [17], corrosion protection [18], [19], [20], [21], [22], [23], coatings [24], [25], [26], [27], [28], sensors [29], [30], [31], [32], [33], [34], [35], energy storage and conversion devices [36], [37], [38], [39], [40], [41], [42], photovoltaics [43], [44], [45], [46], [47], [48], light emitting diodes [49], [50], [51], [52], [53], [54], smart and display technologies and wearable electronics [55], [56], [57], [58], [59], [60], [61], [62], etc.

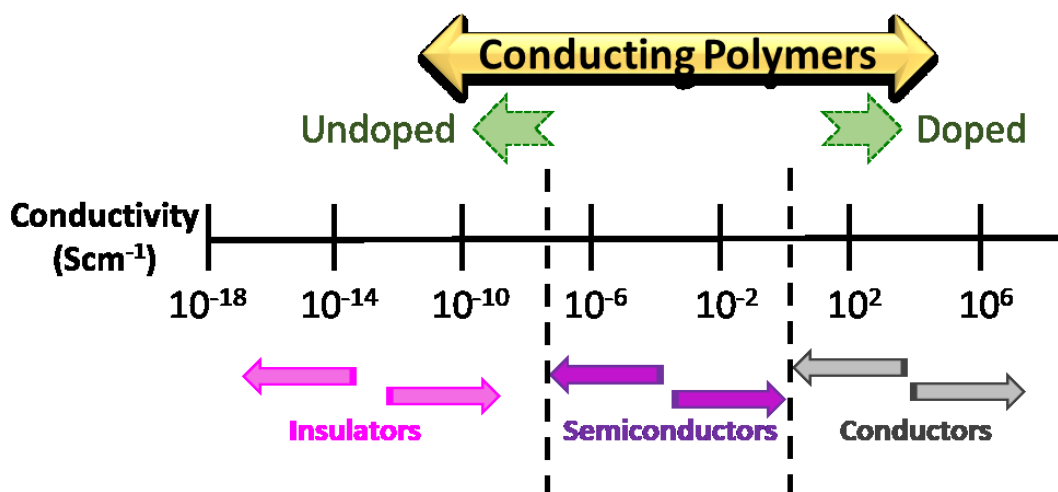


Figure 3. Electronic conducting summary of conducting polymers.

1.2 Polypyrrole: synthesis and characteristics

PPy, formerly known as pyrrole black, was synthesized for the first time in 1916 by Angeli through the polymerization of pyrrole from acidic pyrrole/ H_2O_2 aqueous solution [63]. Its semiconducting behavior was then observed from the leading study of McNeil et al. in 1963 and Dall'Olio et al. in 1968 wherein PPy was obtained through the pyrolysis procedure of tetraiodopyrrole [64], [65], [66] and electrolytic oxidation of pyrrole in H_2SO_4 solution [67], respectively. Great interest was then compelled after the electrochemical synthesis of conducting PPy was applied [68], [69], [70]. Therefore, plethora of PPy studies (more than 30 000 articles) were reported based on Web of Science, making PPy as one of the most studied conducting polymers and used in wide range of applications.

PPy can be strategically synthesized through oxidative polymerization. During polymerization, oxidation of pyrrole takes place, which produces a radical cation. The formed radical cation reacts with another radical cation forming a dimer, which then reacts with another dimer. Meaning, polymerization of pyrrole is carried out in three major steps: oxidation, coupling, and propagation presented in Figure 4 [71], [72]. The oxidation stage can be carried out in different ways: chemical [73], [74], [75], electrochemical [76], [77], [78], and photo-induced oxidation [79], [80], [81]. In chemical oxidation, variety of oxidants can be used like iron (III) chloride (FeCl_3) and ammonium peroxydisulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) to oxidize pyrrole [82], [83], [84], [85]. Applied potential is needed to oxidize pyrrole electrochemically while light is required for monomer oxidation with photo initiator for photo-induced oxidation process. Among these methods, chemical oxidative polymerization is the most common method to synthesized PPy in bulk form. Here, pyrrole and the oxidant are separately dissolved and then mixed together, followed by the formation of precipitates which is then filtered, washed, and dried. The main advantage of chemical synthesis is not only on the ease of preparation but also the polymer is produced in large amount, which is not attainable in electrochemical way.

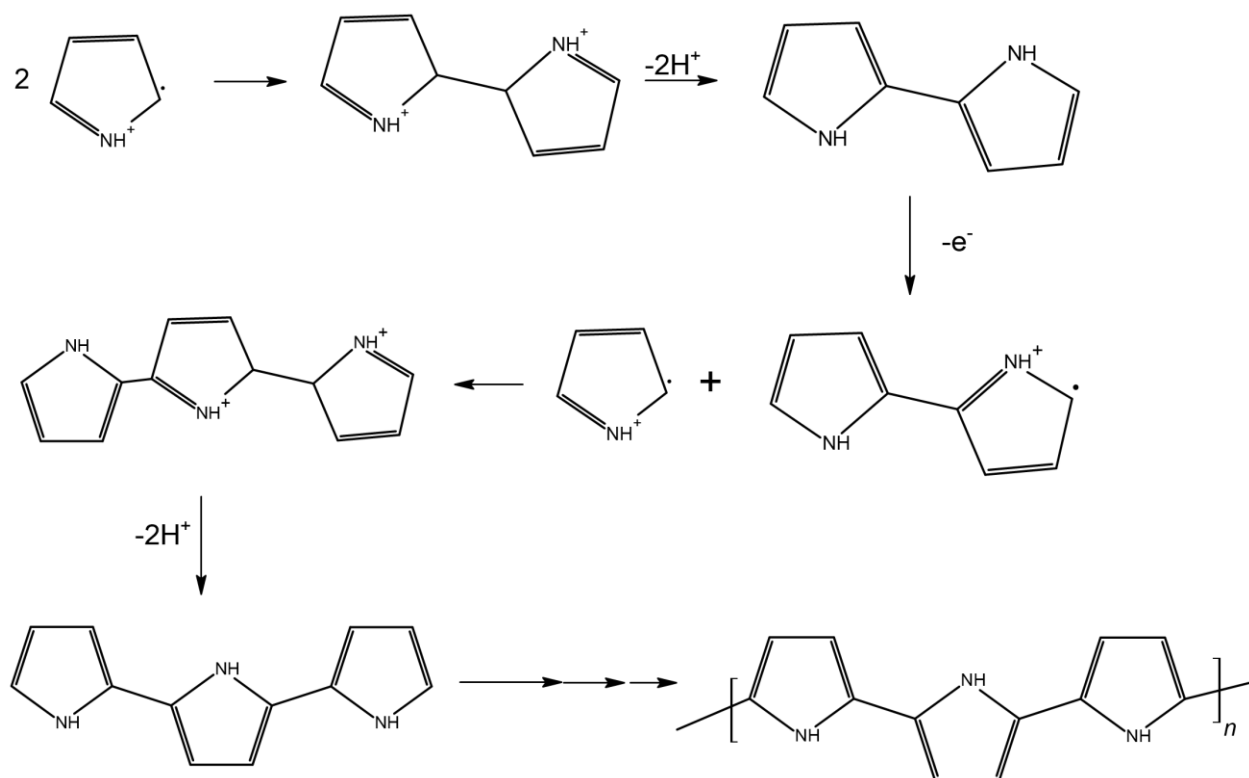


Figure 4. General polymerization mechanism of polypyrrole.

The electrochemical oxidative polymerization of pyrrole can be carried out by applying constant current (galvanostatic) [86], [87], [88], [89], [90], constant potential (potentiostatic) [91], [92], [93], [94], [95], or potentiodynamic (cyclic voltammetry) [96], [97], [98], [99], [100] techniques. These methods are relatively straightforward for synthesizing PPy. Electrochemical polymerization is usually performed in a three-electrode system comprising working, counter, and reference electrodes in a solution containing the monomer, electrolyte, and additives. A lot of crucial parameters are needed to be considered which includes the type of electrolyte, the deposition time or method, and the applied potential or current. All these factors have a substantial influence on the formed PPy film in terms of its morphology, conductivity, mechanical and electrochemical properties, which promptly affects the usefulness of PPy for different applications. Moreover, electrochemical polymerization is convenient way for preparing and characterizing of PPy films or PPy-coated electrodes. Electrochemical oxidation offers a number of advantages such as ease to control morphological structures [101], [102], sequential deposition to produce layered structures [103], [104],

[105], and flexible ability to incorporate dopants [106], [107], [108]. In particular, this method is most preferred to fabricate high-quality PPy films with desired structure and thickness [91], [109], [110]. In the course of electrochemical oxidation, pyrrole is dissolved in solvent with the dopant and oxidized at the electrode surface through the applied anodic potential. Organic solvents (e.g. acetonitrile) or aqueous acidic solution are usually used as medium of polymerization. Table 1 below presents the use of various organic solvents, aqueous acidic solutions and supporting electrolytes during the electropolymerization of pyrrole and the corresponding differences in PPy properties (such as morphology and electrochemical capacitance).

Table 1. Various organic solvents, aqueous acidic solutions and supporting electrolytes used for electrochemically prepared PPy-based materials.

PPy-based material	Solvent	Supporting electrolyte	Electropolymerization method	Electrochemical capacitance	Morphology	Reference
PPy	ACN	Me ₄ NCF ₃ SO ₃	cyclic voltammetry	110 mF cm ⁻²	Granular/Globular	[86]
PPy/PbOx	ACN	TBABF ₄	galvanostatic	249 F g ⁻¹	Globular	[111]
PPy/MnOx/N a-CMC	ACN	TBABF ₄	galvanostatic	343 F g ⁻¹	Globular	[112]
PPy/V _x O _x	ACN	TBABF ₄ /HBF ₄	galvanostatic	522 Fg ⁻¹	Globular	[113]
PPy/CNT	PC	LiClO ₄	galvanostatic	0.451 F cm ⁻²	fibrous three-dimensional reticular structure	[114]
CoN ₄ -PPy	PC/ACN	TBAPF ₆	cyclic voltammetry	721.9 F g ⁻¹	cauliflower-like clusters	[115]
LiClO ₄ - PPy/Ti	ACN	LiClO ₄	normal pulse voltammetry	0.123 mF cm ⁻²	Globular	[116]
PPy/PANI	ACN	Me ₄ NCF ₃ SO ₃	galvanostatic	145 F g ⁻¹		[117]
PPy	ddH ₂ O	KNO ₃	cyclic voltammetry	586 F g ⁻¹	nanosheets	[96]
PPy/Carbon Foam	ddH ₂ O	LiClO ₄	galvanostatic		granular	[118]

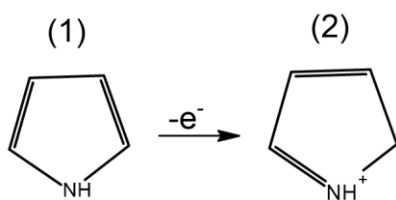
PPy	anhydrous CH ₃ CN	TBAPF ₆	Cyclic voltammetry	~300 F g ⁻¹	nanowires	[90]
PPy/GrO	ddH ₂ O	H ₂ SO ₄	Cyclic voltammetry	642.1 F g ⁻¹	cauliflower-like structures	[119]
PPy/TS	ddH ₂ O	sodium p- toluenesulfona te	galvanostatic	282 F g ⁻¹	Globular	[120]
PPy/CNXL	ddH ₂ O	H ₂ SO ₄	Cyclic voltammetry	336 F g ⁻¹	interconnected nanofibers	[121]
PPy	ddH ₂ O	oxalic acid	Cyclic voltammetry	480 F g ⁻¹	granular/globular	[122]

1.3 Electrochemistry of polypyrrole

1.3.1 Electropolymerization mechanism of polypyrrole

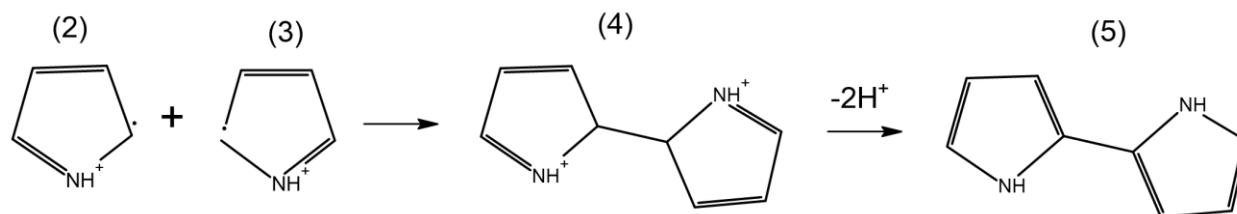
In general, the anodic electropolymerization of PPy involves a series reaction chains of which a polymer film is formed on the electrode surface at the end of polymerization process. The electropolymerization of pyrrole follows several steps of reaction based on Diaz's Mechanism [68], [123]:

Step 1. Oxidation of pyrrole monomer. On this stage, pyrrole monomer oxidizes at the electrode surface forming a radical cation (2) in Scheme 1. Other resonance forms of the cation are also produced and presented in the reaction Scheme 1. The monomers present near the electrode surface undergoes fast oxidation process yielding radical cations which are continuously maintained by the diffusion of monomers to the electrode. Due to the fast electron transfer reactions, the monomers near the electrode surface are in their oxidized form resulting in the production of high number of radical cations and is continually maintained by the diffusion of pyrrole monomers to the electrode with respect to the applied potential. This reaction is followed by the dimerization of the radical cations.



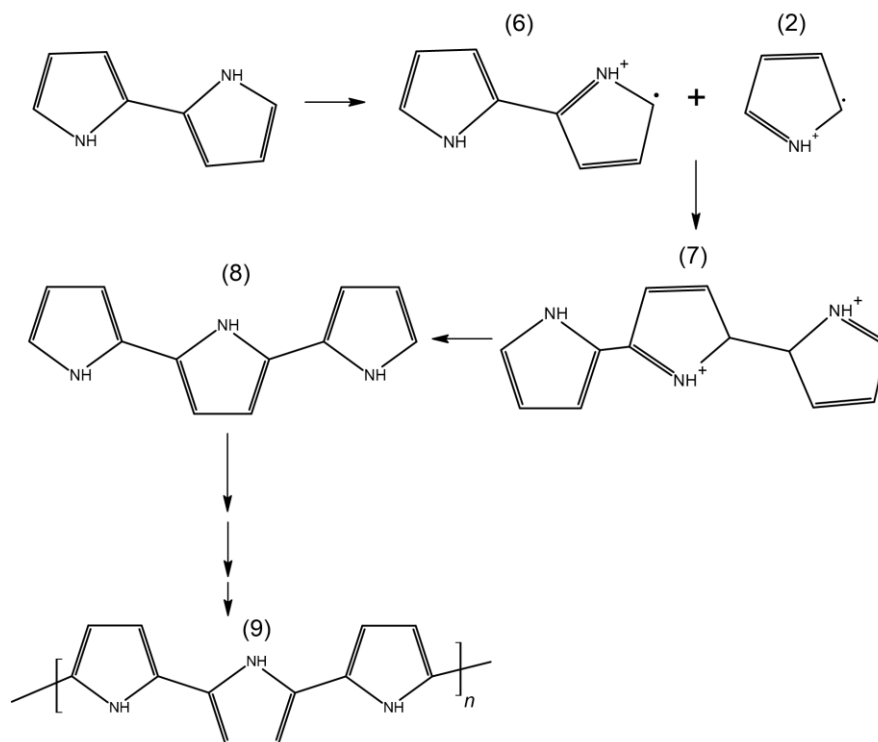
Scheme 1. Oxidation of pyrrole monomer.

Step 2. Dimerization, coupling reactions, and stabilization. The radical cation dimerizes in the α – position after oxidation at the electrode surface. In Scheme 2, the coupling of radicals occurs when bonds are formed at their α – positions yielding dihydromer dication (4). Elimination of protons happens from the doubly charged dimer and produces an aromatic neutral dimer for stabilization. The entire process is illustrated in Scheme 2.



Scheme 2. Dimerization, coupling reactions, and stabilization reactions during the electropolymerization of pyrrole.

Step 3. Oligomerization and chain propagation. Scheme 3 shows the oxidation of the formed dimers into radical cations (6) and then couples to another monomeric cation to form trimer dication (7) which further deprotonates to yield a neutral trimer (8). This is then followed by a series of electro-oxidation and coupling reactions from the cation radicals and create oligomer chains. This propagation continues following the same sequence: oxidation, coupling, deprotonation until the desired polymer (9) is obtained.



Scheme 3. Oligomerization and chain propagation during the electropolymerization of pyrrole.

Aside from Diaz's electropolymerization mechanism, other reported mechanisms such as, Kim's mechanism [124], Pletcher's mechanism [125] and Reynold's mechanism [126] were also presented in literature. Considering Kim's mechanism, pyrrole electropolymerization starts from the loss of a proton and two electrons in pyrrole monomer yielding the intermediate pyrrole radical cation. The growth of PPy is then followed by the simultaneous production of the electropolymerized chains and the nucleation of polypyrrole chains in solution resulting to the tridimensional growth of polymer layer by layer [124]. In Pletcher's mechanism, it was proposed that the formed radical cation couples directly to a neutral pyrrole molecule creating a cation dimer. The cation dimer then loses two electrons and two protons forming a neutral dimer and proceeds to another cation formation and coupling to another neutral pyrrole monomer as the polypyrrole chain propagates [125]. While with Reynold's mechanism, the reaction they presented starts from the formation of radical cations at the electrode surface following the fast growth of chains obtaining a non-conjugated polymer. The conjugated polymer is produced once the polypyrrole is doped by oxidation at the electrode. This mechanism is only limited and valid when conducted in aqueous solutions and with the use of the following electrolytes: ClO_4^- , BF_4^- and PF_6^- [126]. Among all these proposed electropolymerization routes of PPy, the one published by Diaz is considered the most probable based on several experimental investigations [72].

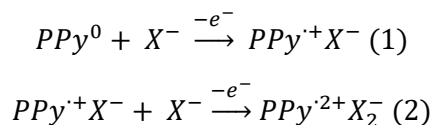
1.3.2. Electrochemical properties of polypyrrole

The electrochemical redox characteristics of polypyrrole mainly involves the oxidation of the π – conjugated system of the PPy backbone. The electrochemical properties of PPy depends greatly on the different electrochemical factors and PPy's characteristics during electrochemical switching. The following factors below confer its effect to the redox activity of PPy:

i. Influence of electrolytes

During the oxidation and reduction of PPy, two simultaneous processes are occurring: (1) the transfer of electrons either from or to PPy; and (2) the diffusion of counterions into or out of the film, respectively. The

redox mechanism of PPy is generally described by the formation of polaronic (1) and bipolaronic (2) units in PPy as shown in the reaction mechanism in Scheme 4:



Scheme 4. Oxidation and reduction reactions of PPy.

According to the scheme presented, upon reduction, anion (X^-) expulsion occurs wherein formation of anionic sites takes place which needs cations for charge neutrality. And when oxidation happens, cationic sites ($PPy^{\cdot+}$, polarons and, $PPy^{\cdot2+}$, bipolarons) are produced following the reaction mechanism [127], [128]. These redox processes can be readily achieved electrochemically.

Typically, the type of the counterion has a strong influence on the PPy's electrochemical performance. The electrochemical capacity in PPy film usually occurs through the redox at the surface or in the bulk and the diffusion of inserted/ de-inserted counterions. In this sense, the ionic conductivity and mobility of electrolyte ions are important in studying the electrochemical properties of PPy. For instance, when the potential is switched on, the PPy film undergoes redox processes as shown in the reaction Scheme 4 and protonated PPy is produced. To preserve the neutrality of PPy chain, the positive charged PPy is balanced by the counterions (or doping anions, X^-) and indicates the principle of *electroneutrality coupling* [128]. This concept refers to the movement of ions into and out of the polymer film in order to maintain charge neutrality. Therefore, when the PPy film undergoes oxidation, the anion, X^- , balances the resulting positive PPy^+ . Some examples of counterions used in studying the electrochemistry of PPy are: nitrates [129], [130], chlorides [131], [132], sulfates [133], [134], phosphates [20], [110], and many more.

ii. Influence in morphology

Changes in the morphological structure of PPy have strong effect to PPy's electrochemical performance especially in terms of the polymer's capacitance and stability. The obtained differences in its electrochemical properties is based on the specific surface area of PPy which solely depends on the

polymer's architecture. Moreover, PPy synthesized through various techniques (e.g. interfacial polymerization [36], [135], electrospinning [136], [137], templating [138], [139]) possess different types of polymer structures resulting to different electronic and electrochemical properties. As such, fabricating PPy nanomaterials with controlled morphology has been greatly considered as it aids to the PPy's overall improvement in electrochemical properties.

Among these methods of preparation, PPy nanostructures can be easily synthesized through templating techniques. This facile method has been proven to be fast and efficient in fabricating PPy with versatile physicochemical and electrochemical properties. During polymerization, these templates act as the structure guiding agent or molds in leading the formation of polymer nanostructures. Most of these templates which have been used in producing nanostructured PPy are: (1) metal oxides like MnO_2 , V_2O_5 , etc. [24], [140], [141], [142]; (2) water soluble polymers or surfactants such as cetyltrimethylammonium bromide (cationic surfactant) [143], [144], sodium dodecyl sulfate (anionic surfactant) [145], [146], poly(vinyl pyrrolidone) [147], [148], [149], [150], [151], poly (vinyl alcohol) [152], [153], [154], [155], etc.; and (3) other additives such as organic dyes (methyl orange, Acid Blue, safranin, methylene blue, etc.) [82], [156], [157], [158], [159], [160], [161], [162], [163], [164], [165], [166], [167], [168], [169]. Therefore, as a promising electrochemical material, PPy's processability is widely explored and studied in order to form nanostructured PPy.

Some PPy morphologies are reported to be like nanodots [170], [171], nanorods [172], [173], nanowires [174], [175], nanotubes [29], [176], [177], [178], and nanofibers [56], [179], [180], [181]. The differences on its electrochemical properties from these different structures depends on the structural uniformity and its effective surface area. The larger the surface area that is in contact into the electrolytic system, the higher is its electrochemical capacitance. Therefore, the influence of morphology is directly related to the electrochemical properties of PPy such as its electrochemical capacitance as presented in Table 2.

Table 2. Influence of various morphological PPy structures to the electrochemical capacitance of PPy.

PPy-based material	Morphology	Surface area (BET), $\text{m}^2 \text{g}^{-1}$	Capacitance	Reference
PPy	nanosheets	37.1	586 F g^{-1}	[96]
PPy/MnO ₂	granular/globules	125	141.6 F g^{-1}	[182]
PPy/graphene	globular	33.5	277.8 F g^{-1}	[183]
PPy/P-Al800	Nanotubes	50	123 F g^{-1}	[184]
PPy-MOF	globular	61.78	263 F g^{-1}	[185]
EGN/PPy	dendritic nanostructures	620	376.9 mF cm^{-2}	[186]
PANI/PPy	nanograins	62	723 F g^{-1}	[187]
PPy/MnO ₂	nanoglobules	123.9	376 F g^{-1}	[188]
MB-PPy	granular	835	572 F g^{-1}	[189]
PPy	nanospheres	17.3	10 F g^{-1}	[190]
PPy/AC	granular	2230	130 F g^{-1}	[191]
PPy/NTs	nanotubes	43.5	109 F g^{-1}	[192]

1.4. Polypyrrole for energy conversion and energy storage devices

Polypyrrole is one of the most attractive conducting polymers for energy conversion and storage devices. It possesses superior electrochemical properties and advantages due to its easy processability and high pseudocapacitive behavior. In recent years, PPy has been extensively studied for energy storage applications such as in batteries and supercapacitors [193], [194], [195], [196], [197], [198], [199]. However, batteries experiences disadvantages such as low power delivery and uptake making supercapacitors a better choice compared to batteries [200], [201]. Hence, this study is focusing on preparing electroactive PPy-based materials for energy storage devices, specifically, for supercapacitor applications.

Supercapacitors are electrochemical devices which bridges the gap between batteries and conventional capacitors. More so, supercapacitors' electrochemical performance operates at a higher specific power than batteries and it exhibits higher energy storage compared to the conventional capacitors [55], [202], [203], [204]. It is an advanced energy storage device having excellent capacitance, fast charge-discharge transfer and long-life cycle [205], [206], [207], [208], [209], [210], [211]. Based on its charge-storage mechanism, supercapacitors are mainly divided into two categories: (a) electric double-layer capacitors (EDLC); and (b) pseudocapacitors. The charge storage mechanism of EDLCs involves non-Faradaic processes wherein it occurs through the adsorption of charges or ions at the electrode/electrolyte interface [212], [213]. Pseudocapacitors, on the other and, behave through reversible Faradaic processes which is demonstrated by the redox reactions between the electroactive material and the electrolyte [213], [214]. PPy-based materials have been utilized in supercapacitor systems as it is very well known for its considerable active surface area, good redox characteristics and high conductivity. And because PPy-based materials can be synthesized in various techniques to produce particular nanostructures, its demand for supercapacitor applications is high. Over the past decade, numerous studies have been carried out to construct nanostructured PPy-based supercapacitors. And many of these nanostructured PPy are used to design an efficient supercapacitor due to the enhanced contact surface area and charge-discharge rate, hence resulting to an improved electrochemical performance. Nanostructures gave PPy-based supercapacitor an advantage to develop and fulfill the demand needed for a high energy storage capacity, better stability (mechanical and electrochemical) and with more functionalities [215], [216], [217], [218], [219], [220]. Table 3 presents various nanostructured PPy-based supercapacitors with its corresponding supercapacitive properties and morphologies which in return shows that PPy provides a noteworthy information that nanostructured PPy plays a significant role for supercapacitors.

Table 3. Various nanostructured PPy-based supercapacitors with its corresponding supercapacitive properties.

PPy-based material	Method of synthesis	Morphology	Capacitance	Energy density	Power density	Capacitance retention	Reference
rGO/PPy NT	chemical	nanotubes	512 mF cm ⁻²	61.4 μ Wh cm ⁻²	10 mW cm ⁻²	86.3%/10 000 cycles	[221]
PPy-Carbon Aerogel	chemical	granules	421.45 F g ⁻¹	52.0 Wh kg ⁻¹	2012.8 W kg ⁻¹	92.81%/5000 cycles	[222]
FEG/PPy-NS	electrochemical	nanosheets	338 F g ⁻¹	48 W h kg ⁻¹	50 kW kg ⁻¹	97%/10 000 cycles	[218]
CNT/PPy-NW	chemical	nanowires	62.5 F g ⁻¹	15.1 W h kg ⁻¹	3000 W kg ⁻¹	72%/3000 cycles	[223]
GF@PA@PPy	electrochemical	bubble paper-like PPy films	527.5 mF cm ⁻²	0.183 mWh cm ⁻³	0.525 mW cm ⁻³	97%/6000 cycles	[224]
Ni@PPy@MnO₂	electrochemical	3D chuzzle-like	168.9 F g ⁻¹	59.8 Wh kg ⁻¹	7500 W kg ⁻¹	84.8%/1000 cycles	[225]
Fe-PrGO	electrochemical	globular	202 F g ⁻¹	61.39 Wh kg ⁻¹	2.5 kW kg ⁻¹	88%/8000 cycles	[226]
ECNT/PPy	electrochemical	core-shell structure	7.24 F cm ⁻³	3.63 mWh cm ⁻³	13.86 mW cm ⁻³	89%/10 000 cycles	[227]

PPy/GO	chemical	porous coral-like	568.35 F g ⁻¹	37.4 Wh kg ⁻¹	75 W kg ⁻¹	83.4%/500 cycles	[228]
PPy/GO	chemical	cauliflower like	931 F g ⁻¹	46.6 Wh kg ⁻¹	469 W kg ⁻¹	84%/1000 cycles	[229]
CNT@PPy@MnO₂	electrochemical	nanosheets	529.3 F g ⁻¹	38.42 W h kg ⁻¹	100 W kg ⁻¹	89.7%/2000 cycles	[230]
PPy-NPipes	chemical	1D nanopipes	107.1 F g ⁻¹	33.5 Wh kg ⁻¹	781 W kg ⁻¹	84.1%/5000 cycles	[231]
GA-hPPy	electrochemical	horn-like morphology	360 F g ⁻¹	8.94 Wh kg ⁻¹	1.2 kW kg ⁻¹	88.2%/10 000 cycles	[232]
CNT@PPy	electrochemical	network structure	281.3 mF cm ⁻²	40 Wh kg ⁻¹	519 kW kg ⁻¹	67.3%/5000 cycles	[233]
PPy	electrochemical	nanowires/nanotubes	443 F g ⁻¹	7 W h kg ⁻¹	75 W kg ⁻¹	94.3%/10 000 cycles	[234]

Traditionally, supercapacitors are constructed using two good performing electrodes and an electrolyte. The electrolytes can be either liquid-based [235], [236], [237], [238] or solid-based [239], [240], [241], [242]. However, for practicality reasons, solid-state supercapacitors are more preferred due to environmental safety, stability, adaptability and flexibility [243], [244]. There are mainly two types of solid-state supercapacitors: (1) symmetric and (2) asymmetric supercapacitors as shown in Figure 5. Symmetric supercapacitors are assembled using identical electroactive materials or layers for both electrodes [245], [246], [247], [248], [249], [250] while the asymmetric ones use nonidentical active materials (which can be composed of an electroactive layer and carbon material for each electrode) [205], [251], [252], [253], [254]. Similarly, nanostructured PPy has been applied for assembling supercapacitors for both configurations as presented in Table 3.

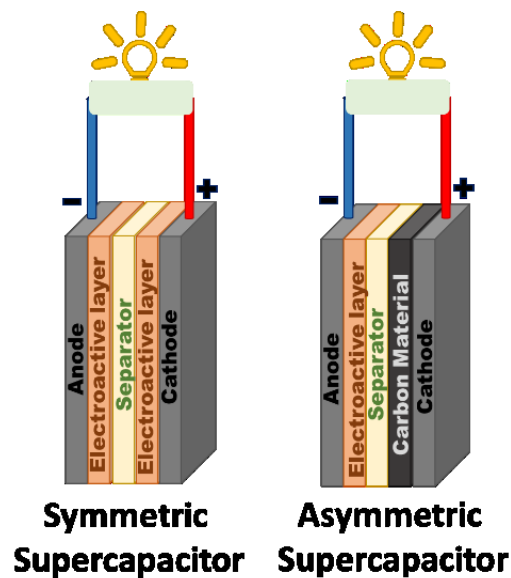


Figure 5. Schematic representation of a symmetric and asymmetric solid-state supercapacitor

Chapter 2 Goals and scope of present study

The main objective of this study is to synthesize conducting-based materials, particularly PPy-based materials capable for energy storage and conversion. The following approaches were used to obtain good electrochemical properties of PPy with enhanced capacitance and energy storage characteristics:

- a. Preparation of PPy films in the presence of various organic dyes (i.e. safranin, Acid Blue 129, Acid Blue 125) via electrochemical oxidative polymerization.
- b. Electrochemical characterization of PPy-based films through various techniques: cyclic voltammetry (CV), galvanostatic charge-discharge measurements, electrochemical cycling stability tests, and electrochemical impedance spectroscopy.
- c. The following other characterization techniques were employed to further study the physicochemical properties of the obtained PPy-based films: Raman spectroscopy, scanning electron microscopy (SEM), Atomic force microscopy (AFM) and X-ray diffraction spectroscopy (XRD).

The other goal of this work is to utilize various PPy-based materials which are prepared chemically in frozen-state conditions for flexible supercapacitors.

This thesis consists of four (4) scientific papers published in international journals with a general introduction and a discussion of the papers' contents.

Chapter 3 Experimental and characterization techniques

Chemicals, reagents, preparation procedures, in addition to instrumentations and measurements techniques are described in detail in the published papers (refer to Appendices). Herein, the basic theories of the various characterization techniques used in the thesis are briefly discussed.

- **Ultraviolet-visible (UV-Vis) spectroscopy**

Ultraviolet-visible (UV-Vis) spectroscopy is a widely known technique in analytical chemistry for quantitative characterization and determination of substances under study. It is a method based on the absorption of light by a given sample. The electromagnetic rays of different wavelengths in the UV-Vis region passes through the sample, and depending on the nature of the sample, light is absorbed partially and the rest is transmitted. The transmitted light is recorded with respect to wavelength representing the UV-Vis spectrum of the sample. The obtained spectrum is then used for various qualitative and quantitative analysis such as identifying the presence of specific components in the sample, determining the analyte concentration in the solution based on the absorbance of light at certain wavelength, and the characteristic information about the molecular structure of the sample represented by the peak positions with respect to wavelength. In this study, UV-Vis spectroscopy was used to determine the presence of safranin-O in PPy. The spectra were recorded using a Lambda 950 spectrometer (Perkin Elmer, UK) by placing the films in the equipment perpendicularly to the incident light-beam of the spectrophotometer.

- **Atomic force microscopy (AFM)**

Atomic force microscopy is a method applied for studying the surface characteristics of a sample by using a sharp tip that is used to scan the surface of the sample through various operating modes: contact modes, dynamic mode or tapping mode. In principle, the nanoscale tip is connected to a cantilever. The cantilever bends when the tip is in contact to the surface and this bending was detected indicating that an interaction between the tip and the sample has occurred. Herein, the AFM experiments for topographic analysis of PPy and PPy/safranin-O on FTO substrates were carried out in tapping contact mode using Nanoscope IIIa

Atomic Force Microscope, Digital Instruments. A silicon cantilever (OTESPA-R3, Bruker) with resonance frequency of 300 Hz, equipped with a tip characterized by a nominal radius of curvature of 7 nm and nominal spring constant of 26 N/m was used. The image processing and roughness analysis of the films were attained by the Nanoscope Analysis software.

- Raman spectroscopy

Raman spectroscopy is a simple, non-destructive technique that is important in analyzing the molecular structure and spectroscopic characteristics of various samples. In principle, Raman spectroscopy is based on Raman effect wherein a monochromatic light passes through the sample and the scattered light is then examined by the spectrometer. The incident light's frequency changes upon scattering and the scattered light shifts up or down depending on the monochromatic frequency. These shifts are then processed and converted into useful data which gives information on the vibrational and rotational transitions in the molecular structure of the sample. In addition, the scattered light greatly depends in the molecular deformations in the molecule caused by its polarizability. Because of these deformations, the vibrating molecules follow a characteristic frequency undergoing Raman shifts. Herein, an Ar-ion 514 nm, HeNe 633 nm and NIR diode laser were used. Three different excitation lines are used depending on the target of study. 785 nm and 633 nm laser lines are in resonance with the electronic transitions including the polarons and bipolarons band in PPy structure while 514 nm excitation line is in resonance with the electronic absorption bands of the dyes used in this study.

- X-ray diffraction (XRD) spectroscopy

X-ray diffraction (XRD) is an all-round non-destructive analytical technique that is used to determine the physical characteristics of materials such as its composition and crystalline structure. In this technique, the x-rays from the source illuminates the sample. As the x-rays hit the sample, it diffracts and enters the detector. When the sample or the detector is moved, the diffraction angle (2θ , angle between the diffracted beam and incident light) changes and the intensity is then measured followed by the diffraction data being

recorded. In this study, the diffraction patterns of PPy-AB25 and PPy-AB129 on FTO substrates were obtained using a high-resolution diffractometer Explorer (GNR Analytical Instruments, Italy) equipped with a 1D silicon strip detector Mythen 1K (Dectris, Switzerland). Sealed X-Ray tube operated at 40kV and 35mA and monochromatized with Ni foil (β filter) was used to produce $\text{CuK}\alpha$ radiation (wavelength $\lambda = 1.54 \text{ \AA}$). Measurements were performed in the range $2\theta = 2 - 40^\circ$ with step 0.1° , with 12s exposure time at each step.

- Scanning electron microscopy

Scanning electron microscopy (SEM) is an all-rounder instrument for investigating and analyzing the morphology and composition of materials being studied. In principle, SEM works based on the generated high energy electron beam that is focused on a probe to scan the sample's surface. The interactions on the sample's surface result to electron emission as the electrons penetrate the surface. The detector then collects the emitted particles and converted to data and information about the sample. This characterization technique grants an immediate observation on the shape, surface morphology and topography of the sample reaching 10000x magnification resolution.

- Electrochemical Techniques

- a. Cyclic voltammetry

As one of the simplest and commonly used electrochemical technique, cyclic voltammetry (CV) is a potential sweep method that offers a good understanding about the electrochemical reactions occurring at the electrode surface and the electroactivity of the active species. In this method, the measurement starts when the initial potential (open circuit potential) is set and a potential sweep occurs at a constant rate (defined by the scan rate in V s^{-1}). This is then followed by another potential sweep on the reversed direction. This potential sweep is set to definite potential window representing the forward (anodic) and reversed (cathodic) direction, respectively. Figure 6, demonstrates the underlying principle in cyclic voltammetry as introduced by Yamada, H., et. al. [255]. In the figure, a reversible one-electron reaction was defined showing

the redox species found in the electrode/electrolyte interface (O, R and e^- refers to the oxidant, reductant and electrons, respectively).

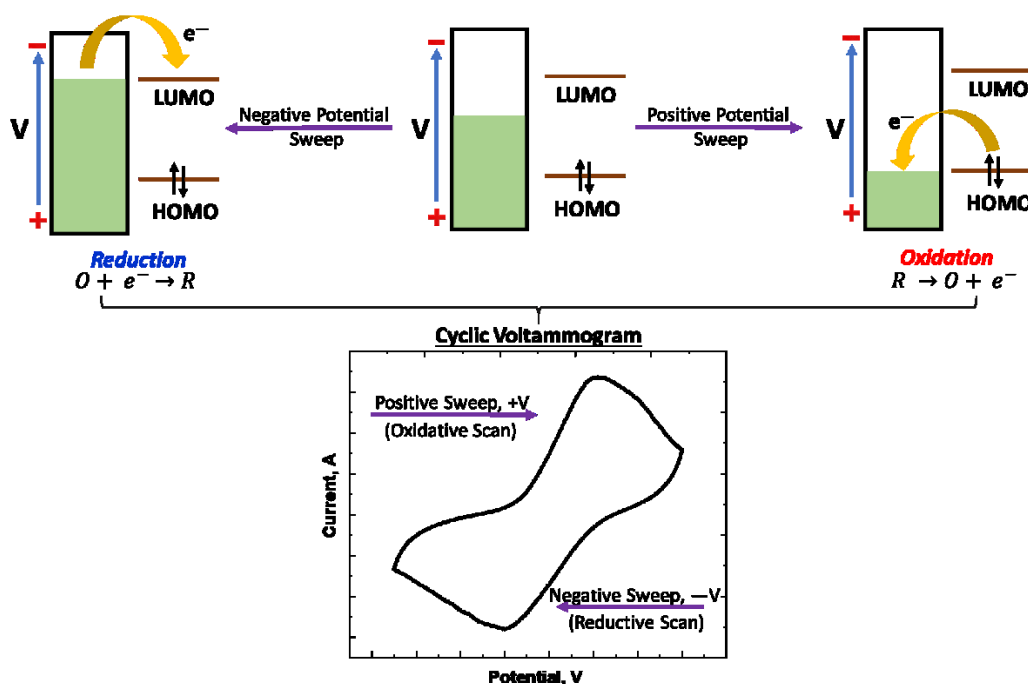


Figure 6. Schematic diagram of the electron transfer during potential sweep on an electrode and the corresponding cyclic voltammogram during measurements, respectively.

During CV measurements, the electrons' energy in the electrode increases as the potential sweeps to the negative direction. This results to the reduction reaction happening in the electrode/electrolyte interface wherein transfer of electrons from the electrode to the electrolyte occurs yielding to R. In reverse, the electrons move to the electrode and oxidation reaction is carried out making the potential sweeps to the positive direction. A voltammogram is usually generated from the CV measurements as shown in the Figure 6. During the oxidative scan, the current increases exponentially as the oxidation begins at the surface of the working electrode. And in reverse scan, reduction reaction occurs which mirrors the oxidation process. Hence, CV is basically used to study the potential during redox reactions of the species in the electrolyte with respect to the changing potential in the electrode.

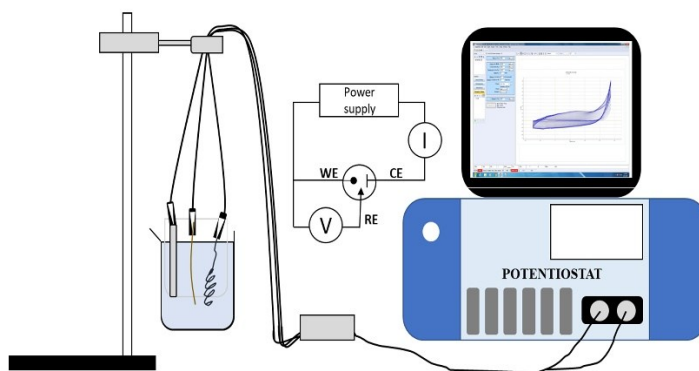


Figure 7. Electrochemical set-up in a three-electrode electrochemical cell.

In this study, the electrochemical deposition of PPy, PPy/safranin-O, PPy-AB25 and PPy-AB129 were undertaken via cyclic voltammetry in a three-electrode electrochemical cell (see Figure 7) with FTO conductive substrate and/or glassy carbon (GC) electrode used as the working electrode, platinum rod as the counter electrode, and AgCl coated Ag wire as the pseudo reference electrode. Moreover, CV was used to examine the electrochemical behavior and determine the capacitance of the synthesized films at varying scan rates. The capacitance of films based on its corresponding voltammograms were calculated using equation 1 below, where, I is the current, v is the scan rate, ΔV is the potential window, and A is the planar area of the film.

$$C = \frac{\int IdV}{2 \times v \times \Delta V \times A} \quad (1)$$

Moreover, the electrochemical properties of PPy-AB25 and PPy-MO prepared in frozen-state ($-24\text{ }^{\circ}\text{C}$) conditions was measured with respect to the mass (m) of the loaded sample on the electrode surface (as described in Appendices A-D) and calculated using equation 2:

$$C = \frac{\int IdV}{2 \times v \times \Delta V \times m} \quad (2)$$

b. Galvanostatic charge-discharge

Galvanostatic charge-discharge (GCD) is a method mostly used to characterized the supercapacitors and batteries because of its straightforward relationship to the capacitance of the material. In this method, the current applied is held constant and the voltage is measured with respect to time against the reference electrode. This method is also called as chronopotentiometry wherein not only the capacitance can be determined, but also long-life cycling, changes internal resistance, and energy and power density. In this technique, the capacitance is calculated based on the charge-discharge curves obtained, showing the amount of charges that the electrodes can store with respect to the discharging time of the stored charges and to the applied voltage. Through this characterization method, the capacitive behavior of materials can be measured in three-electrode or two-electrode set-up. In three-electrode system, the capacitance of PPy-AB25 and PPy-MO synthesized in frozen-state was calculated according to equation 3 presented.

$$C = \frac{I\Delta t}{m\Delta V} \quad (3)$$

In two-electrode system, the set-up is assembled in solid-state as shown in Figure 8. This assembly depicts a supercapacitor device wherein we can investigate further the performance of PPy-MO for supercapacitors. Through GCD measurements, the supercapacitive properties of the constructed device was studied. The capacitance (C_S , F g⁻¹) of the device is calculated based on equation 4. Wherein k is the constant multiplier ($k = 2$ if the mass of a single electrode is used and $k = 4$ if the mass of both electrodes is considered) [256]. The energy density and power density of the device was also determined according to equation 5 and 6, respectively.

$$C_S = k \frac{I\Delta t}{m\Delta V} \quad (4)$$

$$E_S = \frac{1}{2} C_S (\Delta V)^2 \quad (5)$$

$$P_S = \frac{E_S}{\Delta t} = \frac{I\Delta V}{2m} \quad (6)$$

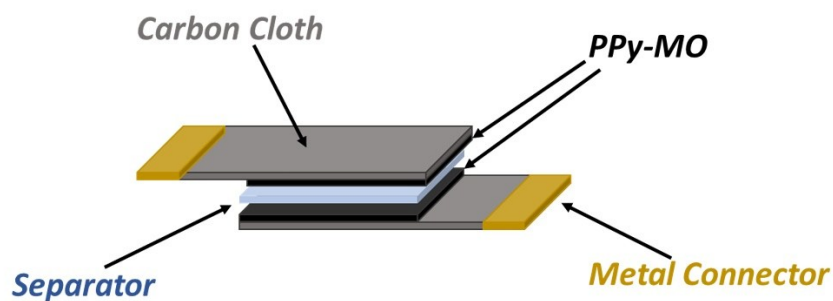


Figure 8. Two-electrode supercapacitor prototype assembly using PPy-MO as the active material.

c. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is a very powerful electrochemical technique wherein it can provide numerous information involving the electrical, electrochemical and physical processes occurring in the system. As defined by Lazanas, A., et.al. [257], EIS is conducted through an applied *ac* voltage or current causing in the perturbation of the electrochemical system in steady state on a wide range of frequencies. The current or voltage response of the system is monitored according to the applied perturbation. More importantly, the obtained EIS spectra can be derived to an equivalent electrical circuit that consists of passive and complicated components (such as resistors, capacitors, inductors, etc.) connected to each other in various ways. This equivalent electrical circuit represents the electrochemical processes occurring in the system that is characterized by various time constants. At low frequencies, slow processes were observed while at high frequencies, fast processes were present, accordingly. Therefore, EIS is considered as a competitive technique for the investigation, optimization, and development of various electrochemical systems for different applications (e.g. fuel cells, batteries, sensors, photovoltaics, and supercapacitors). This characterization method was mainly utilized for PPy-AB25 and PPy-MO in order to further study its electrochemical properties specifically for supercapacitor applications.

Chapter 4 Results and discussion

PPy is widely used in fabricating materials used for supercapacitors. However, due to some PPy's limitations to its electrochemical stability like film swelling and shrinking [119], [216], [258], [259], the requirement to improve its electrochemical performance is still a challenge nowadays. One way to overcome these challenges is to modify PPy's processability in order to obtain nanostructured PPy with high electroactive surface area needed for efficient supercapacitors. Recently, the incorporation of organic dyes during the chemical polymerization of PPy has led to the improvement of PPy's electronic properties. Moreover, the addition of organic dyes during the polymerization of pyrrole has been manifested to control the morphology and improve the conductivity of PPy as established from various studies [82], [160], [162], [167], [260], [261]. The role of organic dyes serves as a self-assembled template in aqueous solutions can be utilized to act as a guide in controlling the growth of PPy structures (such as nanotubes or nanofibers).

Based on these findings, this study opted to incorporate the presence of such organic dyes during the electrochemical polymerization of pyrrole in order to modify PPy's morphology and further improve its electrochemical performance for supercapacitors.

4.1 Electropolymerization of pyrrole with and without the presence of organic dyes

Electropolymerized PPy/safranin-O films coated on glassy carbon electrode were prepared at varying safranin-O concentrations as presented in Appendix A. During the electropolymerization, the current density was observed to be increasing indicating the growth of PPy/safranin-O film on the electrode surface (see Figure 9c). The presence of safranin-O in the PPy/safranin-O films was further affirmed from its spectroscopy shown in Appendix A.

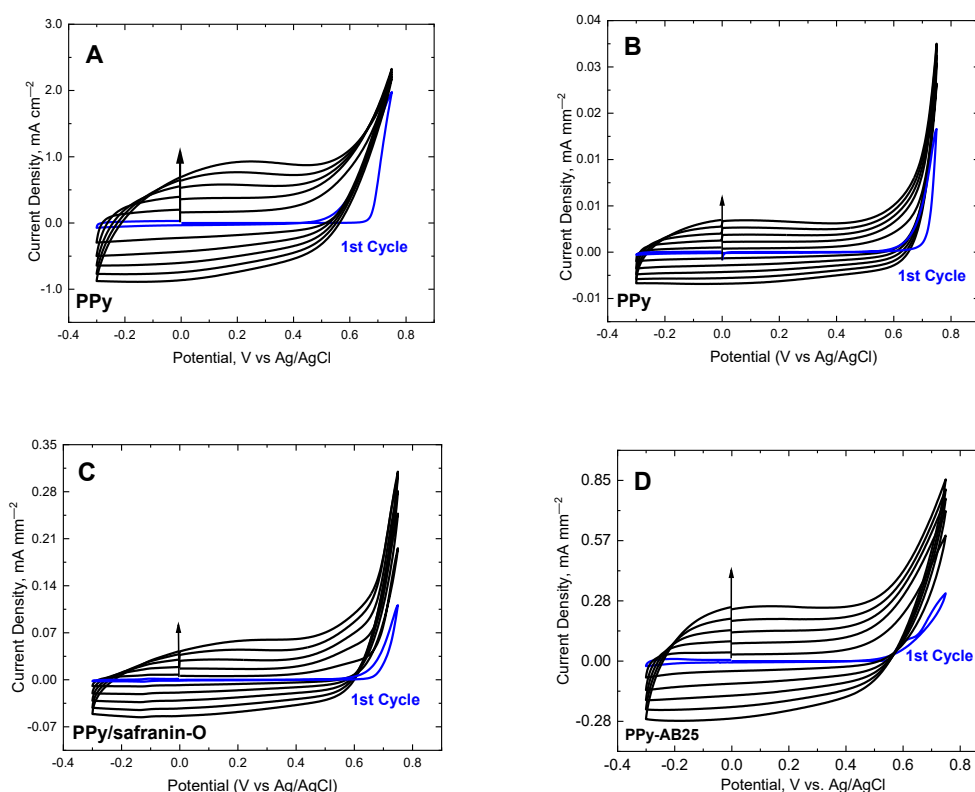


Figure 9. Electropolymerization of pyrrole onto (A) FTO glass substrate (Appendix A) and (B) glassy carbon electrode (Appendix B). Electropolymerization of (C) PPy/safranin-O (Appendix A) and (D) PPy-AB25 (Appendix B) onto glassy carbon electrode.

Moreover, Acid Blue 25 (AB25) and Acid Blue 129 (AB129) were also used as additives in the polymerization of pyrrole and yield PPy-AB25 and PPy-AB129 films coated on FTO glass substrate. Similar to the mechanism of the electropolymerization of pristine pyrrole in Figure 9a, the monomers go through an irreversible oxidation process as observed in the first potential cycle indicated by the blue curves as presented in Figure 10. After the first cycle, the resulting radical cations has served as the nucleation centers accountable for polymer film growth on the electrode surface. As the current density increases for every 5th succeeding potential cycle (black curves), the film grows darker and thicker until the final cycle is achieved. The electrochemical deposition behavior of PPy-AB25 and PPy-AB129 were observed to be

analogous to the growth of pristine PPy film. However, in PPy-AB25, the growth rate is faster with higher current response compared to PPy and PPy-AB129.

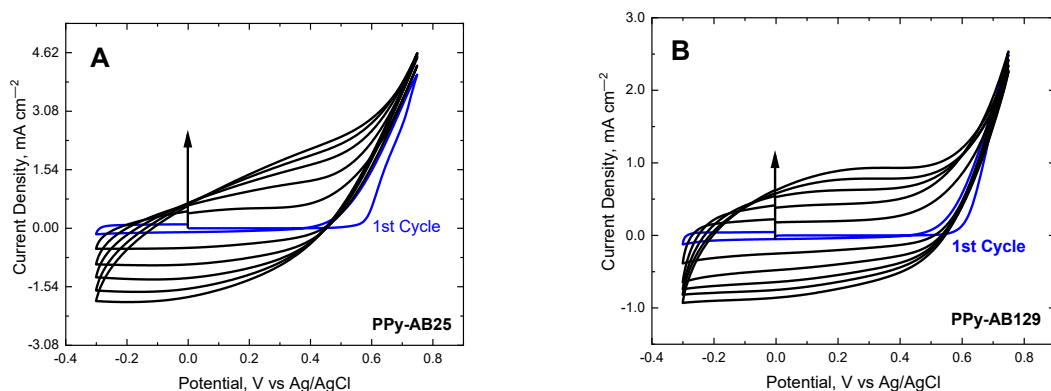


Figure 10. Electropolymerization of pyrrole in the presence of 2.5 mM (A) AB25 and (B) AB129 onto FTO glass substrate (Appendix C).

In addition to this, PPy-AB25 was deposited onto glassy carbon electrode (see in Figure 9d) using the same polymerization electrochemical parameters (refer to Appendix B). And in comparison, to the electropolymerized pristine PPy as displayed in Figure 9b, the growth rate of PPy in the presence of AB25 is faster at higher current density which is similar to growth of PPy-AB25 film on FTO glass substrate (Figure 10a).

4.1.1. The role of dyes on the electropolymerization of pyrrole

In this study, the effect of safranin-O, Acid Blue 25 and Acid Blue 129 on the electropolymerized PPy films were investigated based on the changes in PPy's morphology and on its electrochemical properties which will be discussed later on. The morphology of pristine PPy (presented in Figure 11) have shown globular structures that is typical to PPy characteristics as reported from various studies [260], [261], [262], [263].

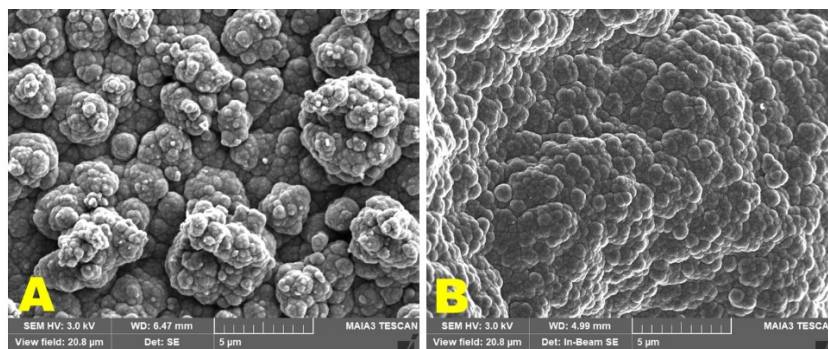


Figure 11. SEM images of electrodeposited PPy onto (A) glassy carbon electrode (Appendix B) and (B) FTO glass substrate (Appendix C) at 10.00kx magnification.

SEM micrographs of PPy/safranin-O films at varying safranin-O/pyrrole w/w% composition ratios were obtained and presented in Appendix A. The SEM images has displayed the appearance of cauliflower-like structures of PPy on its surface. However, the formation of these structures was less pronounced for lower amounts of safranin-O by which they are much similar to the globular structures of pristine PPy. As a result, only small changes in the morphology of PPy were observed in the presence of safranin-O (e.g. the formation of agglomerations on the surface making the structures cauliflower-like and the smaller globular size on the surface). From previous studies, it was demonstrated that safranin-O produces an insoluble precipitate when mixed to iron (III) chloride (which is used as the oxidant for chemically polymerized PPy) [180]. These precipitates are then utilized as a template to control the morphology of PPy yielding to the growth of PPy nanorods. However, in the electropolymerization of pyrrole with safranin-O, the use of an oxidant like iron (III) chloride is not needed and therefore, the production of templates from safranin-O were not possible. In this consequence, the influence of safranin-O in the electropolymerization of pyrrole does not reflect much on the morphology but changes on the electrochemical behavior was observed since an increase in the current density was seen during film deposition. Safranin-O must have facilitated to the fast mobility of pyrrole cations towards the electrode surface following the increase in current response. These observations were further supported by the Raman spectra of PPy/safranin-O films wherein more

bipolarons are present in the molecular structure of PPy indicating an improved order of PPy chains (see Appendix A).

In the presence of AB25 and AB129, regardless that both dyes are of similar structure, during the polymerization of pyrrole two different PPy morphologies were obtained (see Figure 12). AB25 has altered the morphology of PPy to fibrillar one as seen in Figure 12a and Figure 12b. On the other hand, PPy-AB129 films has globular morphology similar to pristine PPy as demonstrated in Figure 12c. Yet, the size of globules is smaller and a secondary globular formation is observed. Further representation of the growth and morphological structures of PPy-AB25 and PPy-AB129 deposited on to FTO substrate were presented in Appendix C.

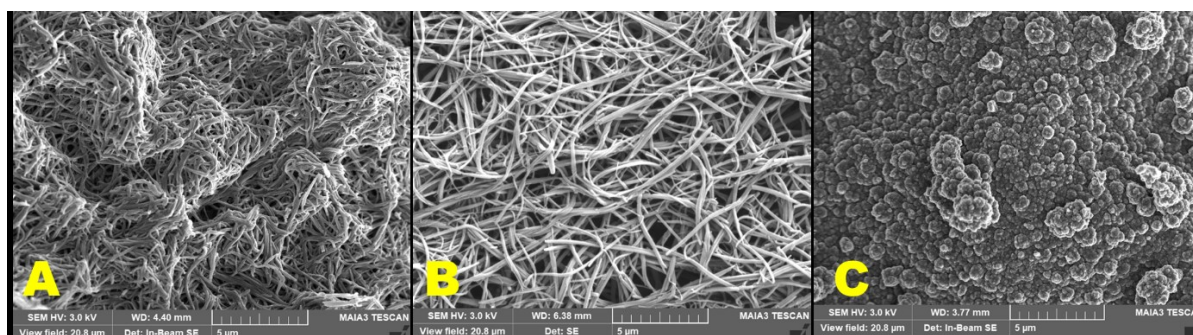


Figure 12. SEM images (10.0kx) of (A) PPy-AB129 and (B) PPy-AB25 grown onto FTO glass substrate (Appendix C). (C) SEM image (10.0kx) of PPy-AB25 deposited on glassy carbon electrode (Appendix B).

It was known that the influence of AB25 in producing PPy fibers is similar to methyl orange dye [163], [264]. Like methyl orange, AB25 forms precipitates or aggregates which separates after its acidification. These aggregates were considered as the templates in forming PPy fibers. With respect to the electropolymerization of PPy, the self-assembled AB25 templates has already formed around the working electrode prior to deposition. Once the potential is applied, the growth of PPy fibers starts to envelope the aggregates. Furthermore, the formation of templates is partially contributing to the higher current response during the electropolymerization of pyrrole. This suggests that the AB25 aggregation aids to the faster diffusion and rapid mobility of monomers while irreversible oxidative reactions are occurring. Therefore,

the templating effect of AB25 has substantially controlled the organization of PPy to form fibers onto the electrode surface.

On the contrary, AB129 does not provide any templates before and during pyrrole polymerization ensuing a globular morphology resembling to pristine PPy. The bulky nature of AB129 has affected the mobility and deposition path of the growing pyrrole cations onto the electrode surface which was evidently observed through the decreased current response during the deposition PPy-AB129.

4.2 Electrochemical characterization

4.2.1. Effect of dyes vs electrochemical capacitance

The films' electrochemical capacitance was determined through cyclic voltammetry at varying scan rates of 10, 20, 50, 100 and 200 mV/s. For PPy/safranin-O and PPy-AB25 films coated on glassy carbon electrode, the areal capacitance was calculated using half of the integrated area of the CV curve with respect to the electrode surface area (7.07 mm^2), scan rate, and potential window (refer to Equation 1). Similarly, the areal capacitance of PPy-AB25 and PPy-AB129 films deposited on FTO glass substrates were estimated based on the films' surface area on the FTO glass substrate which is equivalent to 1.30 cm^2 . Moreover, the electrochemical activity of PPy/safranin-O films were tested in 0.2 M HCl aqueous solution while PPy-AB25 and PPy-AB129 films were measured in 0.2 M HCl, 2 M KCl, and 6 M KOH aqueous solutions.

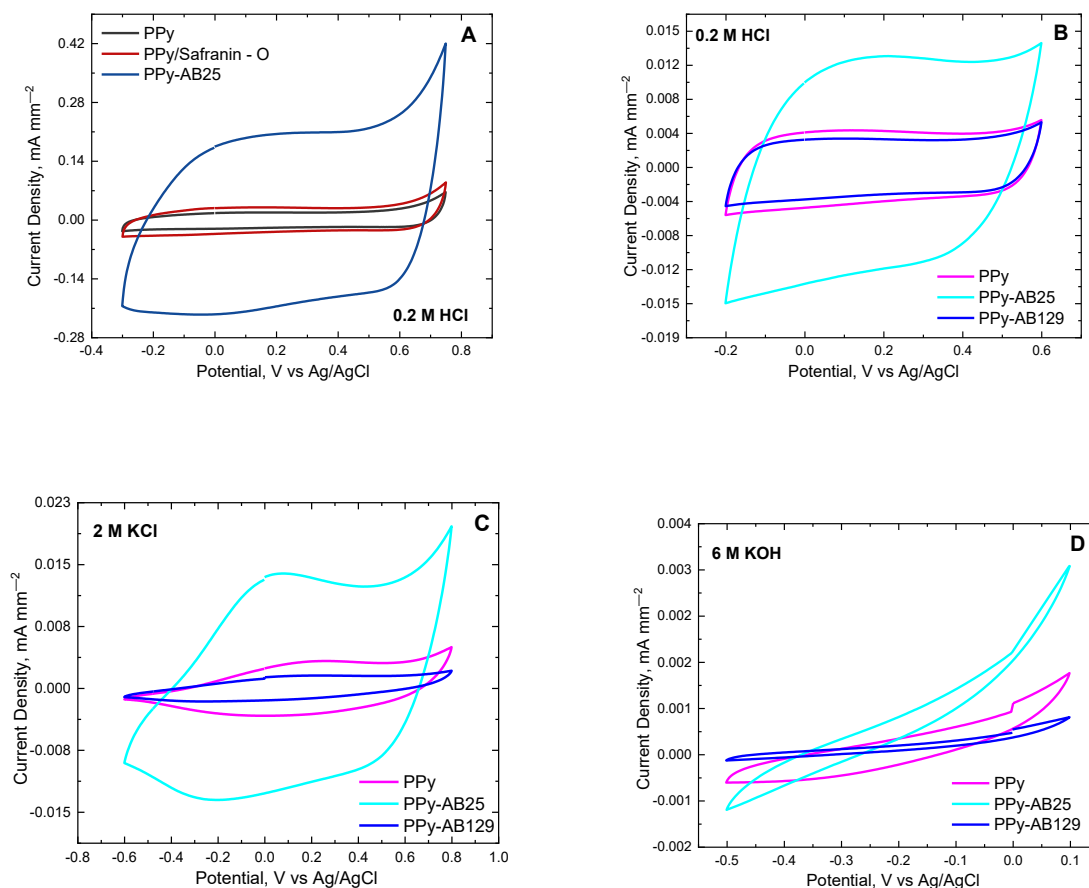


Figure 13. Voltammograms of (A) PPy, PPy/safranin-O and PPy-AB25 deposited on glassy carbon electrode; (B-D) PPy, PPy-AB25 and PPy-AB129 grown on FTO glass substrate measured in different electrolytes (0.2 M HCl, 2M KCl and 6 M KOH).

In the presence of dyes, substantial increase in current density capacity was achieved compared to pristine PPy (see Figure 13 for comparison). These outcomes clearly show that the dyes had a significant influence in enhancing PPy's capacitive behavior. Based on the calculated capacitance, PPy/safranin-O films has notable higher capacitance than PPy film wherein the highest capacitance was obtained for PPy/safranin-O (prepared at 2% safranin-O/pyrrole (w/w%) composition ratio) at 10 mV/s in 0.2 M HCl solution (see in Figure 14). The prepared PPy-AB25 on glassy carbon electrode has a capacitance that is approximately 10

times higher than the pristine PPy. A summary of comparison between PPy, PPy/safranin-O and PPy-AB25 capacitance is shown in Figure 14.

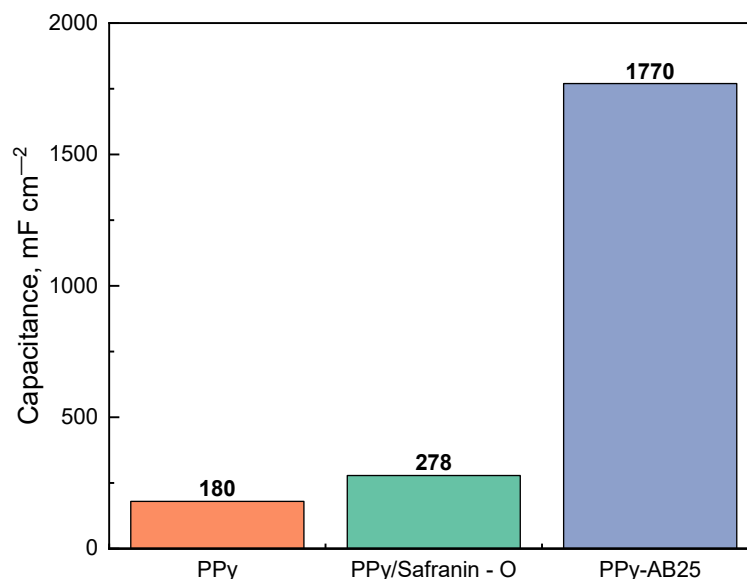


Figure 14. PPy, PPy/safranin-O (2% composition ratio) and PPy-AB25 (with 1.25 mM AB25) films deposited onto glassy carbon electrode.

The capacitive behavior of PPy-AB25 and PPy-AB129 films differs according to the electrolytic solution used during measurements. As a result, the differences in the films' capacitance is increasing following the direction from using KOH < KCl < HCl solution for PPy-AB25 and PPy-AB129. The high capacitance obtained in HCl solution is due to the good conductivity of PPy in acidic medium. While in alkaline conditions, conductivity of PPy decreases and hence, the capacitance has lowered. This can be observed from the poor rate capacity of PPy in KOH solution.

Moreover, PPy-AB25 films has higher capacitance than PPy-AB129 films. This was as expected because the growth rate of PPy-AB25 is faster and at higher current response compared to PPy-AB129 during electropolymerization. In effect, PPy-AB25 film has appeared to be more electroactive than PPy-AB129 in

all electrolytic media used during measurements. Figure 15 illustrates the summary of the calculated capacitance for PPy-AB25 and PPy-AB129 coated on FTO glass substrate.

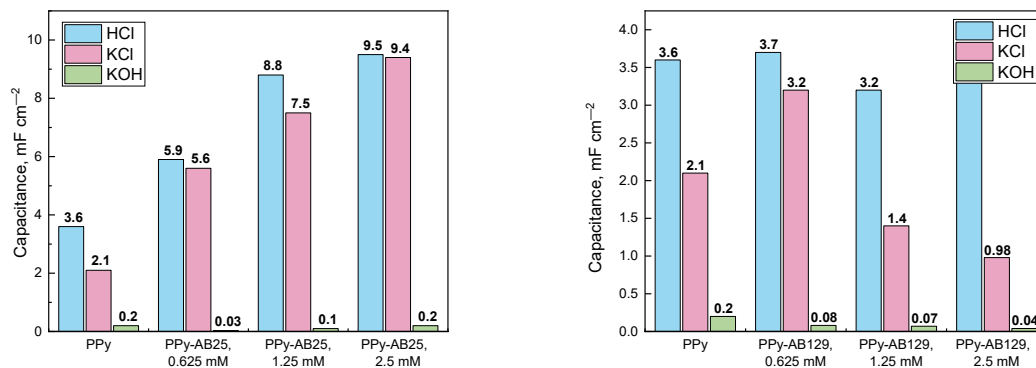


Figure 15. Summary of calculated capacitance for PPy-AB25 and PPy-AB129 coated on FTO glass substrate

4.2.2. Morphology vs electrochemical capacitance

Various PPy morphologies were obtained according to the type of organic dyes which was added during pyrrole polymerization. These differences in the surface morphology of PPy have contributed to the changes of the capacitive behavior of PPy.

In glassy carbon electrode, PPy/safranin-O and PPy-AB25 were electrodeposited. The large difference in its capacitance can be attributed to the different morphologies obtained for PPy as shown in Figure 16. In PPy-safranin-O films, the noticeable formation of cauliflower-like structures has augmented the capacity of PPy. On the other hand, the fibrillar morphology of PPy in the presence of AB25 has caused a large increase in the capacitance by one order of magnitude.

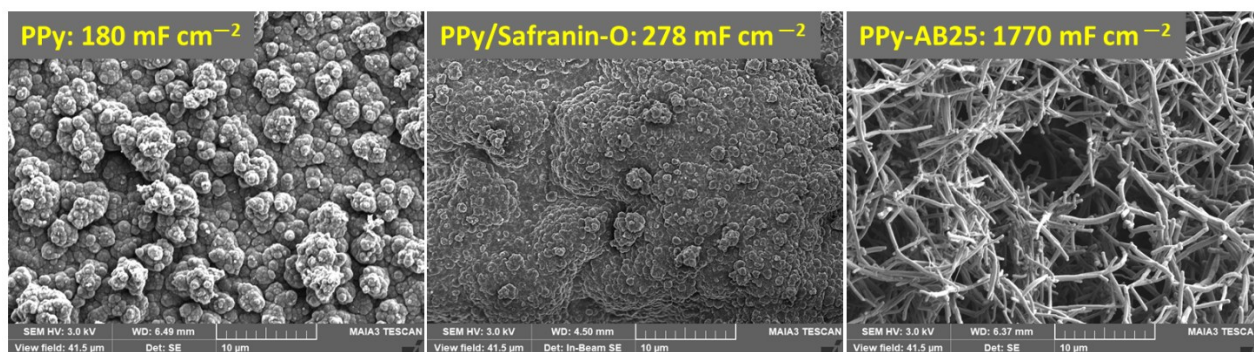


Figure 16. SEM images of electrodeposited PPy (Appendix B), PPy/Safranin – O (Appendix A) and PPy-AB25 (Appendix B) onto glassy carbon electrode at 5.00kx magnification.

For the PPy deposited onto FTO glass substrate in the presence of AB25 and AB129, different PPy structures were observed for both dyes as seen in Figure 17. These differences in the surface morphology of PPy-AB25 and PPy-AB129 showed a significant effect on the capacitive behavior of PPy. Based on the morphological structures of PPy with AB25 and AB129, PPy's size and shape is directly related to the concentration of dyes resulting to the shifting of the charge transfer behavior in PPy. For PPy-AB25, the growth of thinner fibers has apparently increased the capacitance of PPy. This indicates that the diffusion of charges in PPy is faster when PPy fibers are prepared with higher amount of AB25 and subsequently increased the active sites available for charge transfer. Hence, AB25 has improved PPy's capacitance due to its fibrillar structure.

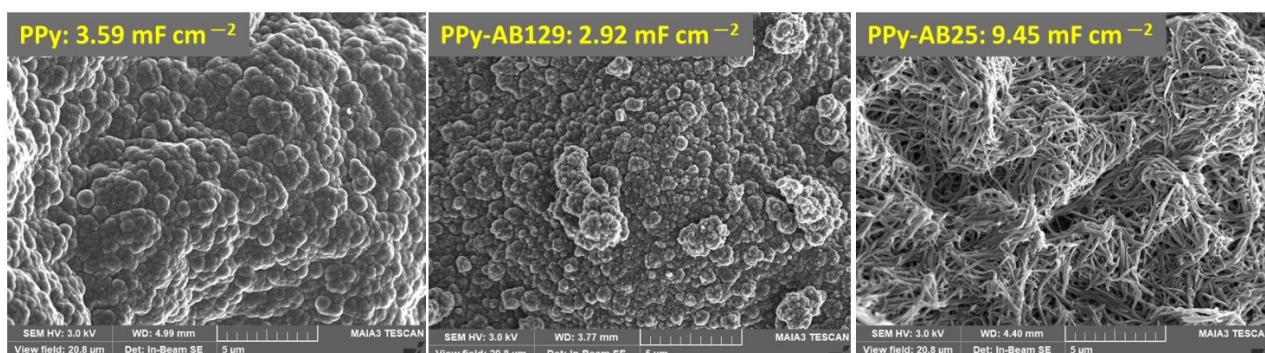


Figure 17. SEM images of electrodeposited PPy, PPy-AB129 and PPy-AB25 onto FTO glass substrate at 10.00kx magnification (Appendix C).

In the case of PPy-AB129 films, there was not much improvement in the capacitance of PPy. This can be entirely due to the similar globular morphology of PPy-AB129 to pristine PPy. Hence, the calculated capacitance values are not too much different to pristine PPy. Therefore, the capacitive behavior of PPy is directly related to its morphology which depends on the preparation of PPy.

4.2.3. Electrochemical stability

The electrochemical stability of the films was evaluated to determine the performance efficiency of the PPy film coated electrodes. PPy/safranin-O film prepared with 2% (w/w%) safranin-O/pyrrole showed the best stability performance (100% retention after 1000 cycles) among the PPy/safranin-O films prepared at varying amount of safranin-O. On the other hand, PPy-AB25 grown on glassy carbon electrode has 89% capacitance retention which is only slightly higher than the pristine PPy (84% capacitance retention). Cycling stability of PPy/safranin-O and PPy-AB25 films on glassy carbon electrode are illustrated in Figure 18.

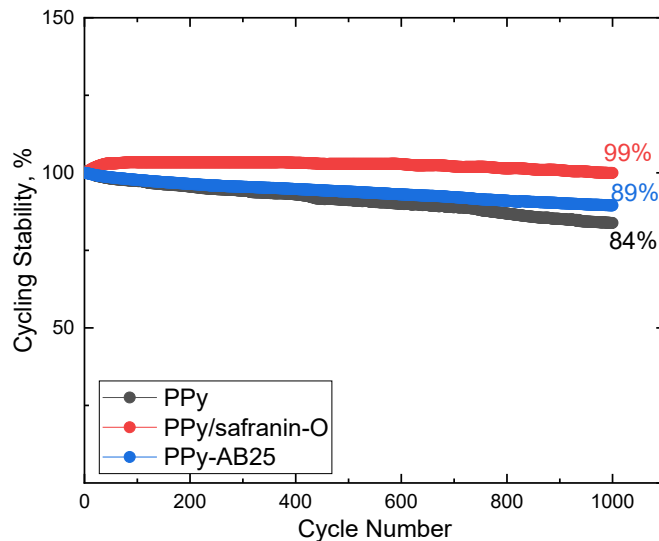


Figure 18. Cycling stability for PPy, PPy/safranin-O and PPy-AB25 films deposited onto glassy carbon electrode (Appendix A and Appendix B).

The cycling performance of PPy-AB25 and PPy-AB129 films deposited on FTO glass substrate were measured during 5000 cycles and presented in Figure 19. After 5000 cycles, PPy-AB129 has maintained its

capacitance at 100% retention while PPy-AB25 exhibited 95% capacitance retention. Both PPy films in the presence of Acid Blue dyes still displayed better performance compared to pristine PPy film coated on FTO glass substrate (93% capacitance retention). Thus, the addition of dyes during the electropolymerization of PPy has helped to improve PPy's electrochemical stability.

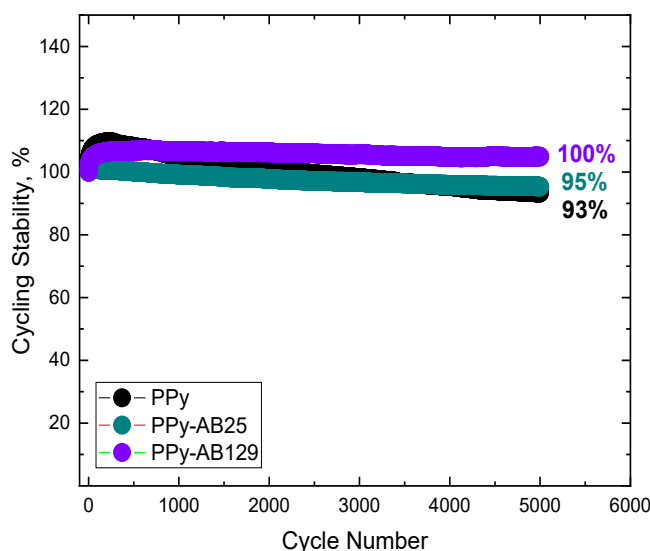


Figure 19. Cycling stability for PPy, PPy-AB25 and PPy-AB129 deposited onto FTO glass substrate (Appendix C).

4.3 Polypyrrole-based solid-state supercapacitors

PPy-based materials have the advantage of being capable of having a high specific capacitance, excellent conductivity, less expensive, and easy to synthesize as they are considered very promising materials for flexible supercapacitors. The only hindrance in using PPy is its low mechanical property and the low electrochemical stability due to swelling and shrinkage during long life cycling [265]. However, recent studies have proven that these inconveniences can be overcome by fabricating nanostructured PPy resulting to higher surface area and porosity [266], [267], [268], [269]. As previously reported by Minisy, I.M., *et al.*, the chemical polymerization of pyrrole with organic dyes in frozen state was found out to produce PPy

nanostructures [181]. Herein, we further investigate the electrochemical performance of the PPy synthesized in frozen-state conditions ($-24\text{ }^{\circ}\text{C}$) in the presence of methyl orange (MO) and Acid Blue 25 (AB25).

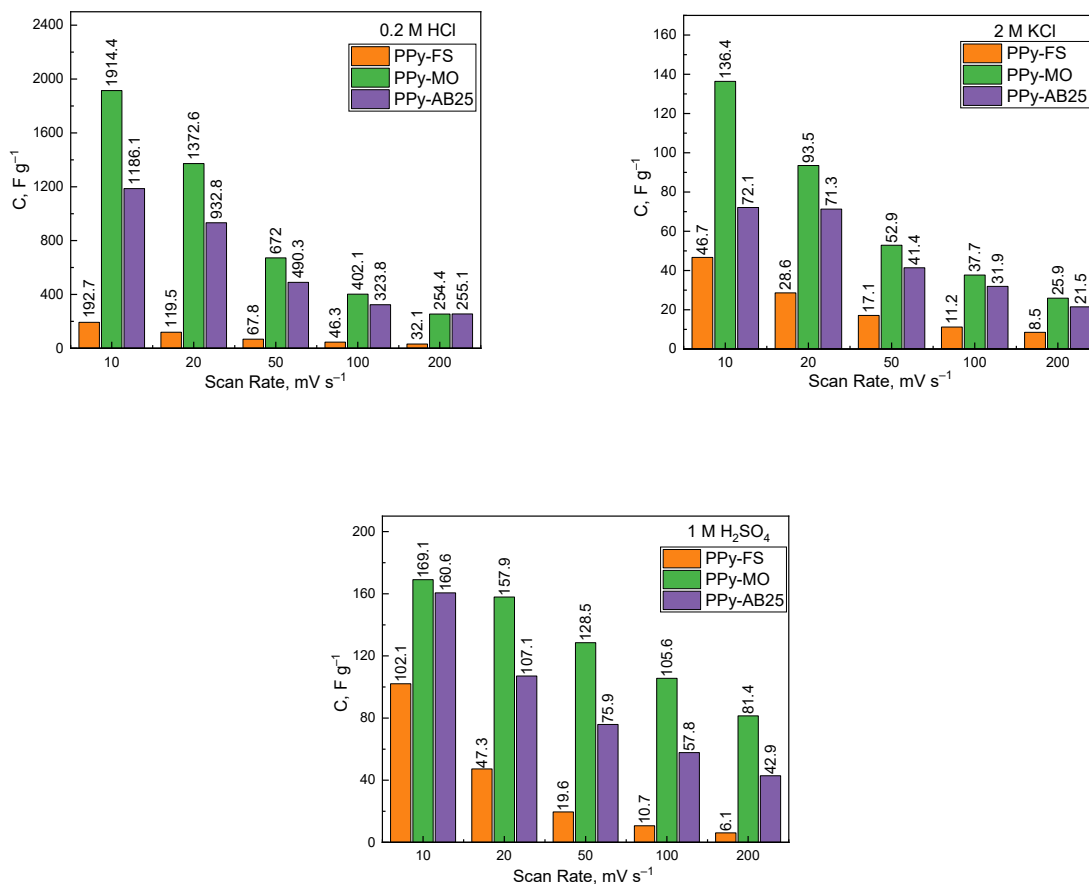


Figure 20. Capacitances based on CV curves at varying scan rates of PPy-based electrodes in different electrolytic media measured in three-electrode system.

In three-electrode system, the electrochemical activity of PPy-MO and PPy-AB25 has significantly increased in all electrolytic media with its capacitance larger than the pristine PPy. The highest capacitance was achieved by PPy-MO at a value of 1914 F g^{-1} (based from CV curve) and 537 F g^{-1} (based from charge/discharge curve) in 0.2 M HCl solution. PPy-MO and PPy-AB25 capacitances that were measured in various electrolytic media showed better capacitive behavior in acidic medium than in neutral conditions as shown in the Figure 20 and Figure 21.

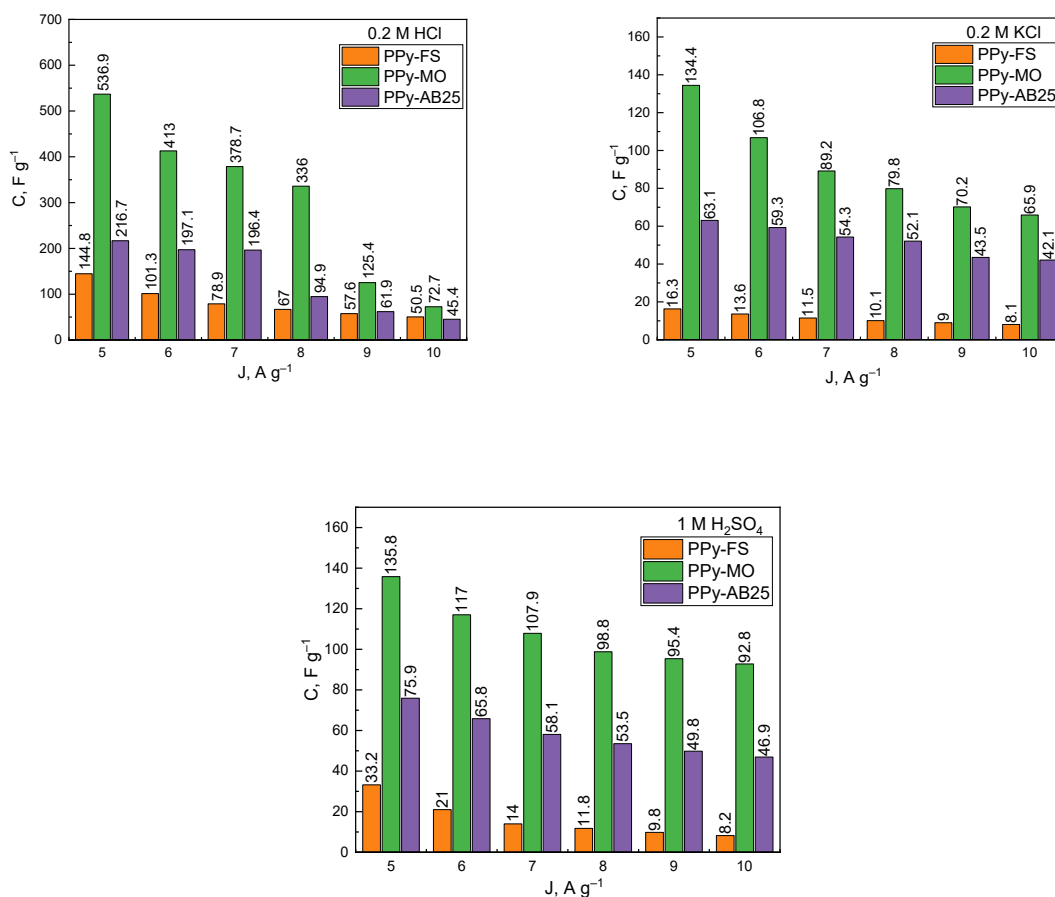


Figure 21. Capacitances based on charge-discharge curves at varying applied current densities of PPy-based electrodes in different electrolytic media measured in three-electrode system.

Also, the presence of MO and AB25 has lowered the charge transfer resistance of PPy which further indicates the increase of PPy's conductivity as presented in the impedance spectra of the PPy-based electrodes (see Figure 22). These apparent improvement in the electrochemical properties of PPy were supported from the Raman spectra (presented in Appendix D) of PPy-MO and PPy-AB25 wherein an increase in the protonation state of PPy was observed in the presence of dyes.

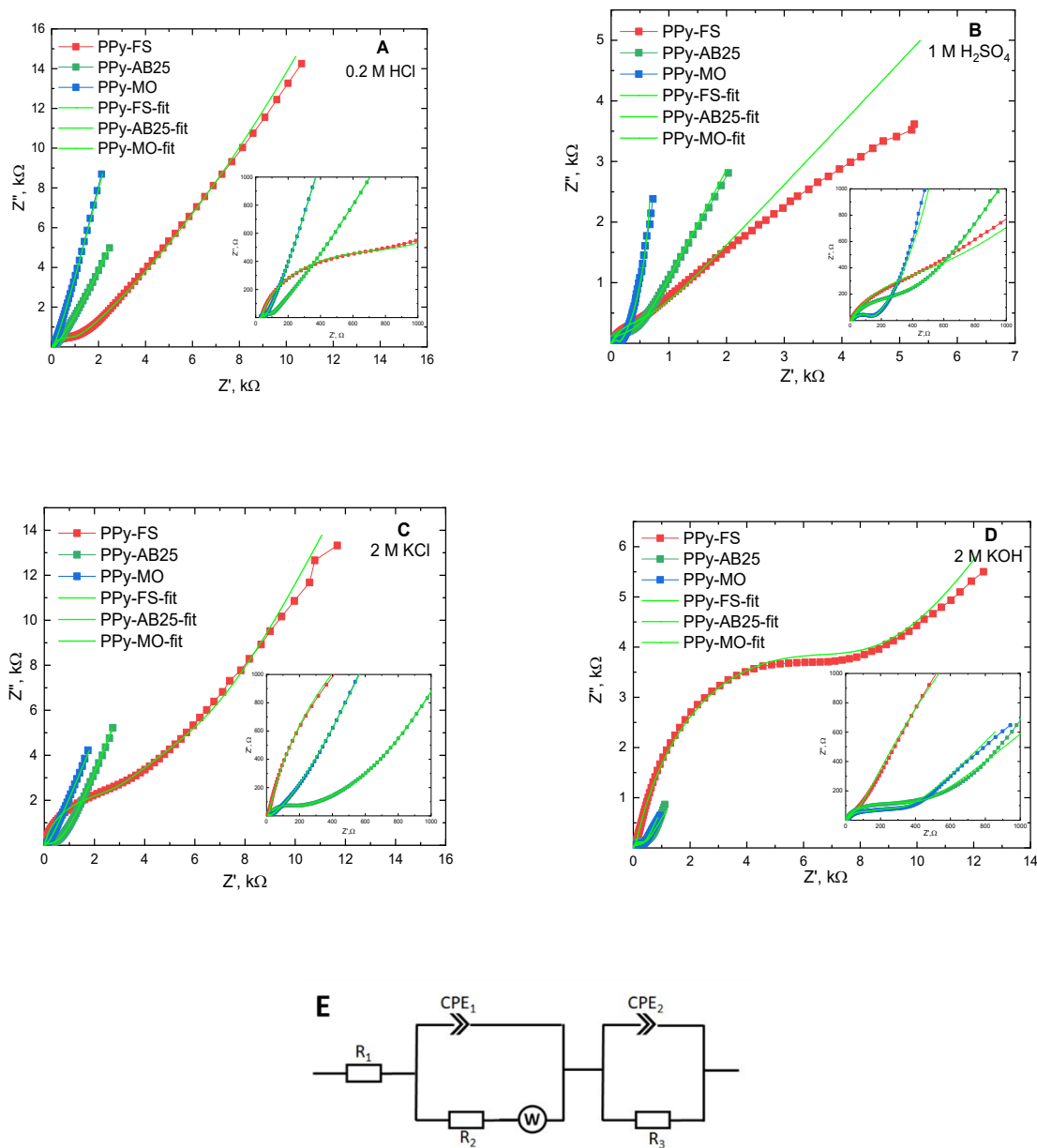


Figure 22. Impedance spectra of PPy with dyes prepared in frozen-state in: (A) 0.2 M HCl, (B) 1 M H_2SO_4 , (C) 2 M KCl and (D) 6 M KOH, respectively and its corresponding (E) equivalent circuit.

Moreover, the frozen-state polymerized PPy-MO and PPy-AB25 are electrochemically stable even after 5000 potential cycling (see Figure 23) which was further reinforced by its stable molecular structure provided by Raman spectra in Appendix D.

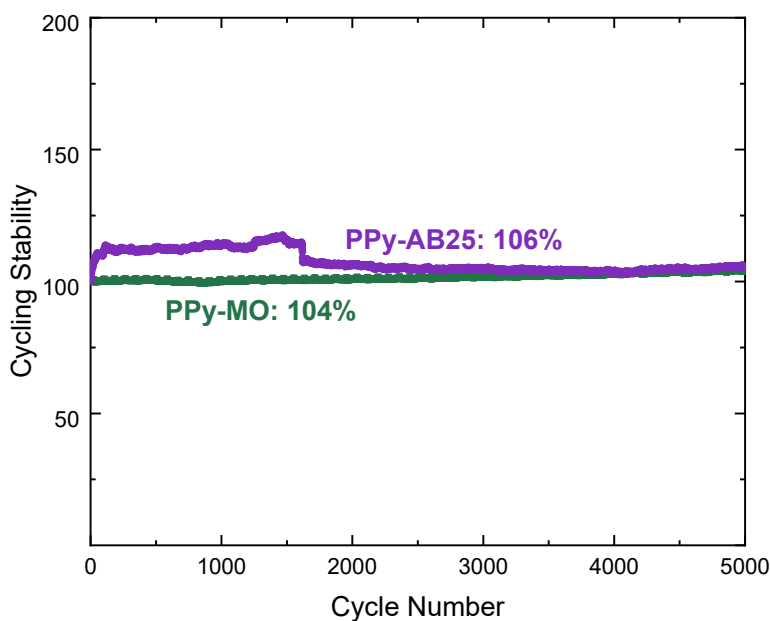


Figure 23. Cycling stability of frozen-state polymerized PPy-MO and PPy-AB in 5000 potentiodynamic cycles (Appendix D).

A PPy-based supercapacitor device was assembled in order to demonstrate the energy storage characteristics of PPy, where it showed good capacitive behavior and stability. The symmetric supercapacitor device was studied through different electrochemical techniques (CV, GCD, EIS, and stability measurements) and a summary of its electrochemical performance is showed in Figure 24. The device's capacitance was calculated with a value of 122 F g^{-1} at 10 mV s^{-1} scan rate and 116 F g^{-1} at 1.5 A g^{-1} applied current density. The energy density and power density of the device were 16 Wh kg^{-1} and 3026 W kg^{-1} at 1.5 A g^{-1} , respectively, and the power density reached up to 9077 W kg^{-1} at 4.5 A g^{-1} . The PPy-MO-based supercapacitor presented good capacitive behavior with a capacitance retention of 89% after 10 000

discharge cycles and exhibited low ESR values and a minimal increase in IR_{drop} values after the long cycling test which was further discussed in Appendix D. All in all, the assembled PPy-MO-based supercapacitor revealed to have efficient electrical and ionic conductivity, and good rate capability for supercapacitors. Hence, this work has demonstrated that the PPy-MO-based electrode is a competent material for fabricating an efficient energy storage system.

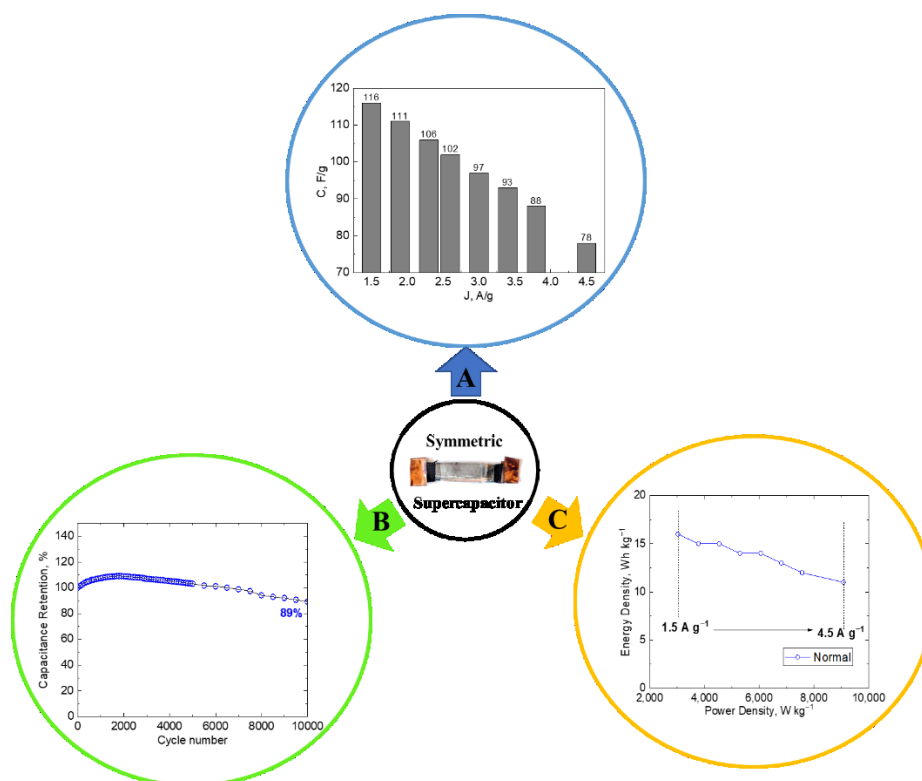


Figure 24. Electrochemical performance: (A) Calculated Capacitance; (B) Capacitance Retention; and (C) Ragone plot of the assembled PPy-MO-based supercapacitor device (Appendix D).

Chapter 5. Summary and conclusions

This work has successfully demonstrated the electrochemical polymerization of pyrrole in the presence of various organic dyes: safranin-O, Acid Blue 25 and Acid Blue 129.

The presence of safranin-O has affected the growth of PPy film into a dense cauliflower-like structures augmenting the electrochemical stability and capacitance of PPy. Meanwhile, the addition of AB25 during the electropolymerization of pyrrole onto glassy carbon electrode influences the morphology of PPy resulting in the formation of fibrillar films. The formation of PPy fibers has enhanced the overall electrochemical performance and capacitance of PPy which manifests a promising material for energy storage devices.

The growth and electrochemical behavior of PPy prepared with AB25 and AB129 onto FTO substrate were also studied. PPy-AB25 appeared to form fibrillar structures while PPy-AB129 contained globular structures. The influence of AB25 dye has notably increased the PPy's capacitance in neutral and acidic solutions whereas AB129 doesn't significantly enhanced PPy's capacitance values. In respect of the film's electrochemical stability, the presence of both dyes, AB25 and AB129, enhanced the retention rate of PPy's capacitive performance. Hence, adding AB25 dyes in PPy production is another way to modify PPy's morphology and enhance its electrochemical performance intended for supercapacitors and other energy storage systems.

In addition, the electrochemical properties of PPy synthesized in the presence of MO and AB25 in frozen - state was investigated and tested its applicability for supercapacitors. PPy-MO exhibited outstanding capacitive behavior in all electrolytic solutions compared to PPy-AB25. Compared to pristine PPy, both MO and AB25 helped in the improvement of PPy's capacitance. This excellent electrochemical characteristic can be attributed to the nanostructured morphology of PPy-MO and PPy-AB25 providing higher electrolyte accessible active sites.

An assembled symmetric PPy-MO-based supercapacitor device was investigated and a good capacitive behavior was observed. The device's performance provided a capacitance retention rate of 89% with low ESR values suggesting a good rate capability and conductivity for the device.

Therefore, the results obtained suggest that modifying the processability and morphology of PPy in the presence of organic dyes (safranin-O, Acid Blue 25, Acid Blue 129 and methyl orange) can be able to fulfill the demands of an efficient energy storage system.

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APPENDIX

- Appendix A.** D. V. Tumacder, I. M. Minisy, O. Taboubi, P. Bober, Highly electroactive frozen-state polymerized polypyrrole nanostructures for flexible supercapacitors, *Polymers*. 2023, 15, 4140.
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- Appendix D.** D. V. Tumacder, Z. Morávková, I. M. Minisy, J. Hromádková, P. Bober, Electropolymerized polypyrrole/safranin-O films: capacitance enhancement, *Polymer*. 2021, 230, 124099.