

Review Article: A Review of Tailoring Polyaniline Ionic Liquids for Long Cycle-Stable Supercapacitors with High Capacitance



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ABSTRACT

Polyaniline (PANI) with tunable morphology was synthesized in ionic liquids to overcome the short cycle life of PANI-based electrodes materials for supercapacitors. It was found that the ionic liquids perform the role of a “soft” template agent and a dopant agent in the polymerization medium of PANI thanks to the non-covalent interactions between the ionic liquids and the PANI. These functions of ionic liquids lead to well-organized nanostructured morphology of PANI and an improvement of PANI-electrode wettability, and thus enhanced electrochemical performances and cycle life stability of PANI-based electrodes. However, the ability of ionic liquids in performing their role either as a soft template or as dopant agent during the PANI synthesis is largely affected by the structure of ionic liquids (head group, alkyl chain length, anion structure, and so forth). This work covers the most relevant studies on the mixing characteristic of PANI and the ionic liquids to gain an insight into the contribution of ionic liquids in controlling the morphology and the related properties of PANI.



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1. Introduction

Polyaniline (PANI) is one of the highest performing conducting polymer used as electrode materials for supercapacitors [1-9]. PANI is characterized with high theoretical mass specific capacitance (~750 F/g in potential range of 0.7 V), a fast reversible doping/de-doping process and controllable conductivity [1-11]. Furthermore, PANI displays excellent chemical and thermal stability, nontoxic properties, ease of its synthesis, and low cost of its monomer [1-7, 10, 12-19]. However, PANI electrodes suffers from lack of cycle life stability (under less than a thousand cycles) in the conventional aqueous acid electrolytes [20-22]. The unsatisfied cycle life stability of PANI electrodes largely depend on its synthesis methods: electrochemical polymerization, interfacial polymerization, chemical oxidative polymerization, and so forth [20, 23-31].

(I) Electrochemical method: the monomer is oxidized at the interface of working electrode, and thus PANI is obtained in the form of a thin film [23-25].

(II) Interfacial polymerization: aniline and oxidant agent are dissolved in two immiscible

phases and the reaction occurs at the interface between these two phases.

(III) “*In situ*” chemical oxidative polymerization: in a standard synthesis protocol, oxidant agent is gradually added into an acidic solution containing an aniline monomer under magnetic stirring to obtain a green powder after filtration, washing with water till pH neutral and drying [20, 27-31].

“*In situ*” chemical oxidative polymerization is the most preferable in terms of productivity. However, it was found that the synthesis conditions (i.e. pH of the reaction medium [32-35], concentration of starting material, temperature, and time of polymerization, stirring conditions [36, 37], size and type of dopant [2, 19, 38-41], type of oxidant [42-44], *etc.* is also a crucial parameter in controlling the morphology and the related properties of PANI. As for the oxidant agent, peroxydisulfate is frequently used as oxidant, and its ammonium salt was favored to the potassium counterpart because of its better solubility in water [11]. Furthermore, ammonium persulfate, in contrast to the other investigated oxidant agent, leads to the PANI formation with excellent yield and without over-oxidation when the molar ratios of ammonium persulfate to aniline is 1.20–1.25

[45]. Concerning the polymerization temperature, it is recommended to carry out this polymerization at low temperature as this reaction is exothermic [35]. In addition, a low polymerization temperature provides PANI of high molar mass [11]. Regarding the pH of polymerization medium, a medium with a good acidity (i.e. with high concentration of the proton in the solution or, more accurately, an acidic medium with $\text{pH} < 2.5$) is required to provide head-to-tail coupling, which leads to the formation of emeraldine salt form (i.e. the conducting and stable form of PANI) [35]. On the other extreme, one concern with using the conventional acidic medium as polymerization medium of PANI (even with $\text{pH} < 2$) is the "agglomerated and inhomogeneous" morphology of PANI resulted in such medium [2, 22, 26, 46-51].

The scientific community has admitted that the PANI morphology is one of the crucial factors that significantly control its electrochemical performances [52]. Indeed, nanostructured PANI with homogeneous morphology is preferred to agglomerated morphology for PANI electrodes as the former provides better electrolyte-electrode contact surface, and thus enhances the diffusion of electrolyte counterion into/out of the polymer [2, 26, 46-50, 53, 54]. Recently, the conventional aqueous acidic medium has been replaced with ionic liquids to obtain nanostructured PANI with homogeneous morphology and controlled particles, instead of agglomerated granular morphology, random stakin nano-cudgel morphology or inhomogeneous fibrillar morphology obtained in the conventional acidic media [2, 46-50].

Ionic liquids (ILs) are defined as "green" solvent with a melting point less than $100\text{ }^\circ\text{C}$. They are salts with negligible volatility, high chemical and thermal stability, high ionic conductivity, low cost, inflammability, and nontoxicity features [14, 15]. Ionic liquids are divided into different subclasses as a function of their structure [55]. Aprotic ionic liquids (AILs) and protic ionic liquids (PILs) are two main subclasses investigated as polymerization medium of PANI prepared via "in situ" oxidative polymerization. AILs are characterized with the absence of the available labile proton, while PILs has labile hydrogen [55-58].

Herein, a study about the effect of the ionic liquids as polymerization media on of the structure, morphology, and electrochemical behaviors of PANI is presented based on the most relevant works.

2. Replacing the Conventional Acidic Media with Ionic Liquids

PANI has successfully been prepared in ionic liquids following the "standard" experimental protocol of aniline oxidation. Briefly, the solution of ammonium peroxodisulfate (i.e. oxidant agent) was added into the solution of aniline at low temperature (i.e. at $5\text{ }^\circ\text{C}$ or at room temperature) [11]. When the reaction going, the color of reaction mixture changes from colorless to green, which is the characteristic color of emeraldine salt form of PANI. It was found that replacing the conventional aqueous acidic media (e.g. HCl and H_2SO_4) with the ionic liquids have delayed the apparition of green color during polymerization [2, 59, 60]. Indeed, after the induction of polymerization the reaction mixture immediately turned green in the conventional acidic media, while the dark green color took several minutes to a half an hour to be observed in some ionic liquids-based polymerization medium. This delay of color change means that the reaction-rate was slowed down [59, 60]. It was reported that the decrement of the reaction rate of PANI, not only leads to the nano structuring of its morphology [59], but also is the reason of the increment of the quinoid ring in PANI, and thus the going up of its protonation level [2].

The aspect of reaction mixture at the end of the polymerization process has also been affected when the conventional acidic media is replaced with the ionic liquids. In the conventional aqueous acidic media, the obtained PANI is precipitated, and it can be collected by filtration [11, 61]. However, in neat ionic liquids, the resulted solution is too viscous and the resulted PANI is not precipitated [2, 45, 59]. Therefore, to collect PANI in form of powders, the product was either dialyzed (dialysis tube, 100 MW cutoff, Fisher scientific) [59], or separated by centrifugal [2]. Furthermore, PANI prepared in neat ionic liquids was collected by pouring the final solution into NaOH solution to precipitate

the polymer followed by filtration [45]. Consequently, PANI prepared in neat ionic liquids is given the label of organo-soluble PANI as it is highly soluble in many organic solvents (e.g. acetone, tetrahydrofuran, dioxane, dimethylformamide, *N*-methyl-2-pyrrolidone, so on) [45, 59]. As for example, 25 mg of PANI powders can be fully dissolved in 1 mL dimethyl sulfoxide [59]. As for PANI prepared in the binary mixture ionic liquid/water, it is precipitated and it can be collected by filtration without any prior treatment similar to what obtained in the conventional acidic aqueous media [46, 48, 62, 63].

As for the chemical structure of PANI, it was not influenced by replacing the conventional acidic media with the ionic liquids. PANI in emeraldine salt form has been obtained whether in the conventional acidic media or in the ionic liquids with an electrical conductivity of about 0.22- 11.9 S/cm at 20 °C depending on the type of dopant [39, 46, 61].

3. Doping PANI with Ionic Liquids

Doping PANI means the incorporation of impurities into its backbone in order to increase its charge carriers that leads, not only to an improvement of its electrical conductivity, but also to control its surface wettability [59, 64],[49]. **Figure 1** details the effect of doping, also known as protonation, on PANI structure according to the literature [11, 16, 19, 65]. As it showed, doping transforms the PANI from its emeraldine base EB form (i.e. insulating form with $\sigma \sim 1.4 \cdot 10^{-8}$ S/cm or 6.10^{-11} S/cm) to its conductive form (emeraldine salt ES form). Briefly, a unit of PANI in the EB form has two benzenoid amines (-NH-) and two quinoid imines (=N-). The latter with pK_a of 2.5 can be easily protonated with the free protons

available in the medium, inducing the formation of PANI positively charged. The electroneutrality of charged PANI is maintained with the counter ions of the medium, and thus, PANI in ES form is resulted [66-68].

Fourier transform infrared FTIR analysis is generally used to distinguish PANI base form from its salt form since most of the absorption bands shifts to the lower frequencies when PANI is converted from base form to the salt form [70, 71]. This shift is attributed to the fact that doping enhances the charge delocalization and leads to the formation of conjugation structure of PANI [70].

As for PANI prepared in the ionic liquids, some characteristic vibration bands of the ionic liquids were detected on the FT-IR spectra of PANI, revealing that the ionic liquids was not removed from the backbone of PANI during its purification [59, 62]. In other words, the characteristic vibration bands attributed to the ionic liquids on the FT-IR spectra of PANI demonstrate that PANI is doped with the ionic liquids. In the same context, Stejskal *et al.* reported that the fully undoped insulating base form of PANI (its electrical conductivity is about 6.10^{-11} S/cm) has become electrically conducting (with an electrical conductivity of about 0.43 S/cm) after mixing it with 1-ethyl-3-methylimidazolium [49]. This increment of electrical conductivity reveals that PANI is protonated with the ionic liquid [49]. On the other extreme, it was reported that some ionic liquids are easily washed out of PANI during its purification since no modification has occurred on the FT-IR spectra of the resulted PANI, as compared with the typical PANI [2, 46, 63].

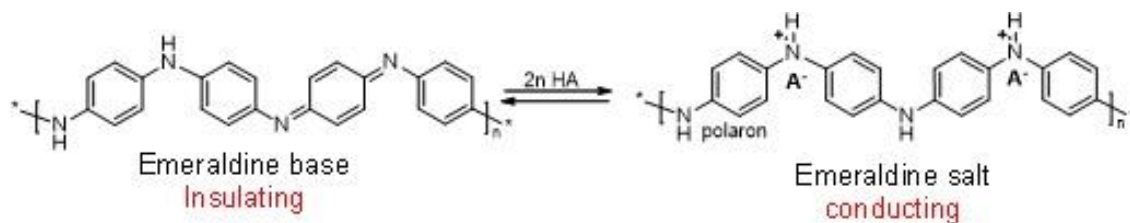


Figure 1. PANI transformation between its base and salt form

Doping PANI with ionic liquid (IL-PANI) due to the non-covalent possible interactions between the ionic liquids and PANI [2, 46, 49, 59, 62, 63, 69, 70]. Error! Reference source not found. summarizes these possible interactions according to the type of ionic liquids. For comparison, the interaction between PANI and the ordinary Brønsted acid is also listed in Error! Reference source not found.. Here are the main possible interactions according to the nature of the polymerization medium:

3.1 Ordinary Brønsted acid

Brønsted acid protonates PANI via covalent bond. Briefly, acid dissociated in water produces free protons, which interact with the lone pair electrons on an imine nitrogen $-N=$ to form a covalent bond.

3.2 Disubstituted imidazolium-based ionic liquids

Although disubstituted imidazolium salt has non-available proton and resistant to hydrolysis, it can dope PANI via non-covalent interactions [49, 69, 70]. As summarized in **Table 1**, imidazolium salt acts as Lewis acid and accepts the electron located on imine nitrogen of PANI, leading to hydrogen bond between imine nitrogen of PANI and hydrogen atom in the 2-position of imidazole. Note that the size or the nature of substituent of imidazolium ring can favorite or prevent this interaction [62].

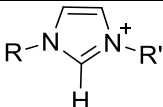
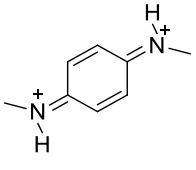
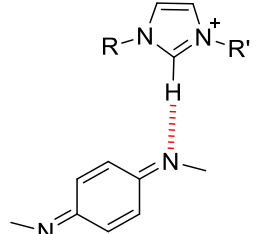
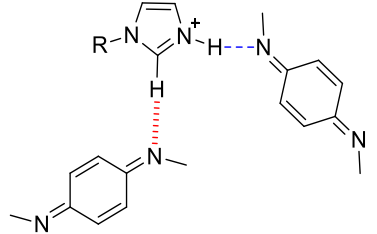
3.3 Monosubstituted imidazolium-based ionic liquids

This type of ionic liquid acts as Brønsted acid and Lewis acid when doping PANI [59]. Like disubstituted imidazolium, monosubstituted imidazolium interacts with PANI through the hydrogen atom located on the 2-position of imidazolium ring. Furthermore, monosubstituted imidazolium through its available proton can also interact with PANI. Note that it was found that hydrogen bonds act as a cross-linking agent and reduce the inter-layer spacing between PANI chains [59].

3.4 Non-substituted imidazolium-based ionic liquids

PANI with nanostructured morphology was successfully prepared in imidazolium hydrogen sulfate [71]. As confirmed by ATR-IR analysis, most of the characteristic bands of the PANI were shifted to lower wavenumber when replacing the conventional acidic medium (*i.e.* HCl) with this ionic liquid. This shift was attributed to the interactions between imidazolium hydrogen sulfate and the PANI. However, the type of these interactions have not studied and identified although that the resulted PANI exhibited higher electrical conductivity and better electrochemical performances as compared with the PANI prepared in disubstituted imidazolium-based ionic liquids.

Table 1. Recapitulation of the interactions between Brønsted acid, disubstituted, or monosubstituted imidazolium and the PANI

HA (<i>e.g.</i> HCl, H ₂ SO ₄ , ...)			
	R & R': alkyl groups	R = alkyl group R' = H	R = R' = H
Ordinary Brønsted acid	Disubstituted imidazolium	Monosubstituted imidazolium	Non-substituted imidazolium
			
	AIL acts as Lewis acid	IL simultaneously acts as Lewis acid and as Brønsted acid	Its role is not clear yet

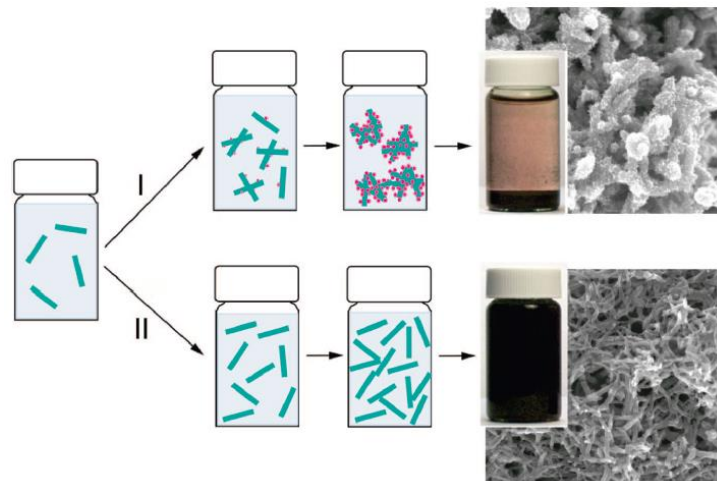


Figure 2. Schematic illustration of the nucleation mode of PANI and typical SEM images resulted from each polymerization mode (I) heterogeneous nucleation mode and (II) homogeneous nucleation mode (data are reproduced with permission from reference [38]), copyright 2006, American chemical society).

4. Controlling Morphological Characteristics of PANI Using Ionic Liquids

The PANI morphology goes from irregularly agglomerated particles to nanofibers structure or homogeneous spherical particles when the ionic liquids were added into the polymerization medium [2, 26, 59, 63]. This radically change of PANI morphology was attributed to the nucleation mode: Homogeneous or heterogeneous mode. **Figure 2** provides a schematic illustration of the nucleation mode. The difference between these nucleation modes is observed as the polymerization proceeds with time. For homogeneous nucleation, the well-dispersed nanofibers PANI are continuously produced (Route II), and thus homogeneous PANI fibers are resulted. However, for the heterogeneous nucleation, the new polymerized PANI grows on the performed PANI (Route I), leading to the formation of agglomerated morphology of PANI.

The ability of ionic liquids as polymerization medium in nano structuring PANI morphology was interpreted with its role as a “soft template agent” [2, 46, 48]. This role has been confirmed in the work completed by Li *et al.* based on the field scanning electron microscopy FESEM images of PANI obtained at different reaction time [2]. It was shown that 1-ethyl-3-

methylimidazolium salt is the self-assembled molecules, which direct formation process of PANI particles when the polymerization is going. Indeed, this ionic liquid directs PANI morphology formed as follows: the anions of the ionic liquids adsorb on the surface of the positively charged PANI and form a layer, and thus the cations of the ionic liquids move to the outer layer, leading to the formation of spherical PANI particles. On the other extreme, the formation of nanostructured PANI in ionic liquids has also been possible thanks to the non-covalent interactions between PANI and the ionic liquids [46, 49, 59, 69, 70]. **Figure 3** displays the possible non-covalent interaction between PANI and the imidazolium salt. The hydrogen interaction might be either between imidazolium nuclei and PANI or between the secondary amino group of PANI and the anions of the ionic liquids [49, 59, 70], presented as number 1 and 2 on **Figure 3**. Hydrogen bond is known as a cross-linked agent, which induces the formation of a cross-linked porous structure and interconnected network of PANI chains [59]. Furthermore, PANI can interact with the imidazolium salt through π - π interactions, presented as number 3 in **Figure 3**. This type of interaction can direct the effect of the structure of head group of the ionic liquids, as presented in the following paragraph [46].

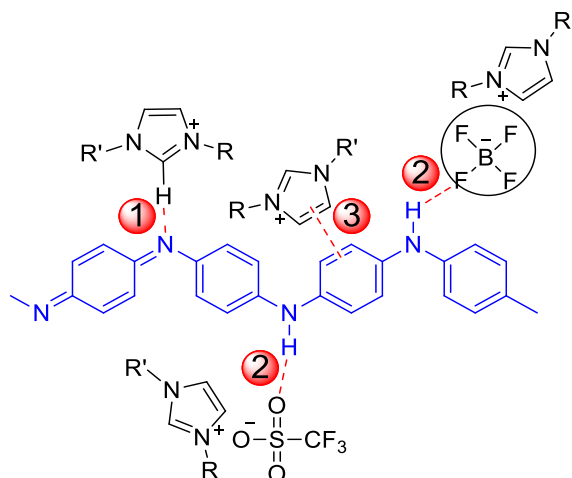


Figure 3. Possible interactions between PANI and imidazolium salt: (1) hydrogen bond between imine nitrogen of PANI and hydrogen atom in the 2-position of imidazolium, (2) hydrogen bond between secondary amino group in PANI and anion of AIL, and (3) π - π interaction between PANI and 1,3-dialkylimidazolium cation (adapted with permission from reference [55], copyright 2022, ISSN 2737-5323).

On the other extreme, the efficiency of the ionic liquids in controlling PANI morphology during synthesis strongly depends on the structure of ionic liquids and the aniline/ionic liquids mole ratio [2, 45, 46, 48, 62]. Here are some examples:

- **Head group structure**

PANI was successfully prepared in acidic aqueous solutions of 1-butyl-3-methylpyridinium chloride, 1-butyl-3-methylimidazolium chloride or methyltributylammonium chloride [46]. PANI with nanowire particles was obtained in 1-butyl-3-methylpyridinium or 1-butyl-3-methylimidazolium chloride (*i.e.* ionic liquids with monocyclic unsaturated rings; asymmetrically disubstituted imidazolium, disubstituted pyridinium), while lamellar morphology of PANI was resulted in tetraalkylammonium-based ionic liquids [46]. The difference between the resulted morphology of PANI was correlated to the possible π - π interactions between the head group of the ionic liquids and PANI. The non-covalent interactions between PANI and imidazolium or pyridinium ring leads to the formation of PANI with nanostructured fibrillar morphology. However, the absence of such interaction between ammonium nuclei and PANI gives PANI with lamellar particles.

- **Aniline/ionic liquids mole ratio**

It was reported that the PANI morphology prepared in 1-butyl-3-methylimidazolium

chloride [bmIm]Cl is strongly related to the mole ratio of aniline/[bmIm]Cl [48]. Homogeneous nanowire with a defined diameter (80-100 nm) of PANI particles was obtained when aniline/[bmIm]Cl mole ratio is 1/1. However, when the mole ratio of ionic liquid is less or greater than that of the aniline, the PANI morphology is a mixture of nanowire/granular or granular/lamellar particles.

- **Alkyl chain length in ionic liquids**

Nanostructured PANI with maize-like nanorods morphology was prepared in aqueous solution of 1-alkyl-3-carboxymethylimidazolium chloride with different alkyl chain length [62]. It was found that increasing the length of alkyl chain led to the decrement of the number of maize-like nanorods that might be because of the role that alkyl chain length plays in the physicochemical properties of ionic liquids.

- **Anionic part of ionic liquids**

PANI prepared by the assistance of 1-ethyl-3-methylimidazolium bromide or tetrafluoroborate ([emim][Br] or [emim][BF₄]) displayed spherical morphology [2]. Both [emim][BF₄] and [emim][Br] play the role of surface growth directing agent for PANI. However, replacing Br⁻ by BF₄⁻ anion decreased the size of PANI particles from 100-120 nm to 50-80 nm because of the less hydrophilicity of BF₄⁻ [2].

5. Enhanced Electrochemical Behaviors of IL-PANI vs. the Conventional PANI

PANI-based electrode materials for supercapacitors, like the other conducting polymers-based electrodes, exhibit pseudo capacitive behaviors [62, 72-77]. In other words, PANI electrodes store electrochemical energy mainly through surface faradaic redox reactions, normally accompanied with the adsorption/desorption of electrolyte anions at the electrode/electrolyte interface. As electrode materials for pseudo capacitors, PANI is considered as promising candidates since it can afford higher charge density as compared with the expensive metals oxide and the other conducting polymers. However, one concern with PANI-based electrodes is its short cycle life. Indeed, during cycle life test, the intercalation/deintercalation of the ions of electrolyte into/out of PANI chains leads to the swelling and shrinkage of PANI material, and thus to the degradation of PANI performances [20-22].

Replacing the conventional PANI with that prepared in ionic liquids (i.e. IL-PANI) provides enhanced electrochemical performances and better cycle life stability. The enhancement of electrochemical performances and the cycle life stability of IL-PANI are attributed to the power of ionic liquids on nanostructuring of PANI morphology synergistically with an improvement of the wettability of IL-PANI electrode [2, 59, 62, 63]. In this section, we discuss the reason behind the enhancement of the electrochemical performances of PANI prepared in the ionic liquids.

5.1 Faradaic transition of PANI during electrochemical transition

It is primarily important to review the faradaic transition of PANI between its different oxidation states during electrochemical characterization via cyclic voltammetry in a three-electrode mode of PANI electrodes is generally. This technique is well-known in showing the faradaic process of PANI [72, 76, 78]. **Figure 4a** shows the typical cyclic voltammogram curves adapted from reference [26]. It was obtained in 1 mol/L HClO₄ using a

three-electrode system configuration consisted of PANI loaded on Au plate (2×2 cm) as working electrode [26]. A platinum plate and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively [26]. From **Figure 4a**, it is clear that PANI-electrodes display the pseudo-capacitive behavior as two pairs of reversible redox couple were observed. The redox couple located at 0.05 V vs. SCE is attributed to the reversible transformation between leucoemeraldine base and emeraldine salt forms. At more oxidizing potentials (at about 0.75 V vs SCE), the second redox couple is obtained and associated to emeraldine/ pernigraniline couple. Sometimes, the so-called middle peak appears, revealing the presence of *ortho*-coupled polymers or the degradation of PANI into benzoquinone/hydroquinone couple [20, 52, 59]. **Figure 4b** reviews the reversible transformation between the different oxidation states of PANI during the electrochemical characterization. The transformation between the leucoemeraldine base and emeraldine salt forms (i.e. the first redox couple observed on the cyclic voltammogram) involves only electron transfer [54, 79, 80]. In other words, the transition from Leucoemeraldine base to Emeraldine salt means an electron is lost per a dimer aniline rings in PANI. Thus, PANI becomes positively charged and counterion of electrolytes diffuse to its surface to maintain the electroneutrality. The counterion diffusion into/out of PANI depends on the morphology of PANI and it is the best in the case of shaped-controlled nanostructured PANI [26]. The second redox process (i.e. emeraldine/ pernigraniline couple) involves both electron transfer and proton transfer [79, 80].

Cyclic voltammetry profile of IL-PANI is similar to that of the conventional PANI, revealing that ionic liquids have not affected the faradaic redox process characteristic of PANI-based electrodes [2, 63, 81]. As for the area under the cyclic voltammogram, it is much larger in the case of IL-PANI, indicating that IL-PANI provides higher specific capacitance.

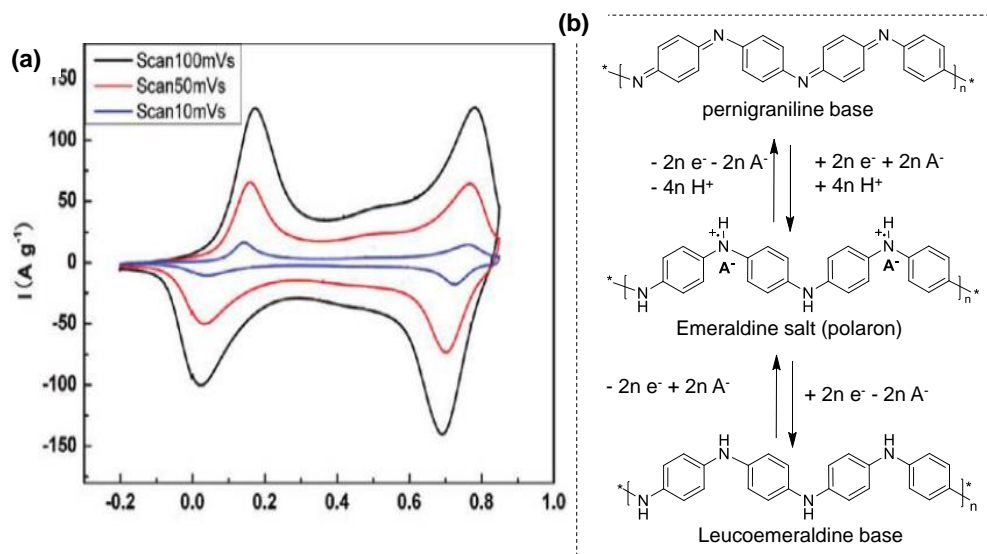


Figure 4. (a) Typical cyclic voltammogram profile of PANI electrodes in conventional aqueous acid electrolytes and (b) Faradaic transition between different oxidation states of PANI ((a) is adapted with permission from reference [27]; copyright 2010, American chemical society and (b) is reproduced with permission from reference [85], copyright 2013, ISSN 2079-4991).

5.2 Dependence of electrochemical performances of IL-PANI on its morphology

The relationship between PANI morphology and its electrochemical performances has been reported in the work completed by Li *et al.* [2]. They prepared PANI in 1-ethyl-3-methylimidazolium having either bromide or tetrafluoroborate anion (*i.e.* [emim][Br] or [emim][BF₄]) and compared its electrochemical performances with the conventional PANI. Note that IL-PANI (*i.e.* PANI-1 and PANI-2) exhibited spherical morphology, while the conventional PANI (*i.e.* PANI-3) had random stacking nanocudgel morphology. **Table 2** summarizes the size of PANI particles and the electrochemical performances of the resulted PANI. The electrochemical studies were carried out using a three-electrode configuration system in 6 mol/L KOH. A slurry of PANI: acetylene black: polyvinylidene fluoride with a ratio of 85:10:5 was loaded on titanium mesh (1*1 cm) and used as working electrode. The counter electrode and reference electrode were a platinum sheet and a saturated calomel electrode, respectively. As depicted in **Table 2**, IL-PANI displayed higher specific capacitance

and better capacitance retention as compared with the conventional PANI. The specific capacitance was of about 625, 520, and 342 F/g for PANI-2, PANI-1, and PANI-3, respectively [2]. This improvement of the specific capacitance was attributed to the nanostructured morphology of IL-PANI. Indeed, it is well-known that homogeneous nanostructured morphology of IL-PANI facilitate the penetration of electrolyte counterions into the inner layer of IL-PANI as compared with the agglomerated particles of the conventional PANI. As a result, nearly the whole surface of the IL-PANI-based electrode materials were used [2, 26]. Another point to note from **Table 2** is that the most performing material was PANI-2 thanks to its smaller particles size (*i.e.* the diameter of PANI-2 particle was almost half of that of PANI-1). Indeed, small particles can shorten the charge transport distance in the PANI materials [2]. To conclude, IL-PANI displays enhanced electrochemical performances since it has shape-controlled nanostructured morphology confirmed by the other reported studies [2, 26, 59, 63].

Table 2. Recapitulation of PANI particle size, specific capacitance, and capacitance retention at 0.1 A/g in KOH (6 mol/L) of PANI prepared using [emim][Br], [emim][BF₄] or water

Sample abbreviation	PANI-1	PANI-2	PANI-3
Polymerization medium	[emim][Br]	[emim][BF ₄]	water
Morphology	Spherical particles	Spherical particles	Random stacking nano-cudgel
Particle size (nm)	100 - 120	50 - 80	Agglomerated particles
Specific capacitance at 0.1 A/g in 6 mol/L KOH	520	625	342
Capacitance retention (%) at 0.1 A/g over 2000 cycles	87.5	90.5	74.9

5.3 Electrode wettability

Wettability, introduced as the capability of a liquid to maintain contact with a solid surface, is a crucial parameter in electrochemical field [82-85]. It has been demonstrated that improving the electrode wettability goes along with the capacitance. Indeed, improving the electrode wettability promotes an increment of the rate of used specific surface area of the electrodes, and thus, the penetration of the electrolyte into the porous electrode is facilitated [84, 85]. As for PANI, like the other conducting polymers, it is possible to tune its surface wettability through doping it with a suitable dopant agent with different amount [64, 83]. For example, doping PANI with sodium dodecyl sulfate SDS can change its surface from hydrophobic to hydrophilic [64].

Regarding the hydrophilic ionic liquids incorporated inside PANI chains (*i.e.* IL-PANI), it was suggested that these ionic liquids can improve the wettability of PANI electrodes. Indeed, it was reported that IL-PANI displays an enhanced electrochemical performances as compared with the conventional PANI thanks to many factors, including the hydrophilicity of the ionic liquids [59, 62]. For example, the specific capacitance of PANI doped with 1-vinyl-3-carboxymethylimidazolium chloride (VCMIm)Cl@PANI (*i.e.* 624 F/g at 1 A/g) was almost the double of that of PANI doped with 1-methyl-3-carboxymethylimidazolium chloride (MCMIm)Cl@PANI (*i.e.* 331 F/g at 1 A/g), while the specific capacitance of the conventional PANI was only 216 F/g at 1 A/g [62]. With the vinyl in ionic liquids, IL-PANI (*i.e.* (VCMIm)Cl@PANI) materials experienced higher specific capacitance and excellent

capacitance retention (*i.e.* 94.6% over 1000 cycles at 1 A/g). This remarkable enhanced specific capacitance of (VCMIm)Cl@PANI was associated, not only to the boosted electrode wettability of IL-PANI, but also to the possible non-covalent interactions between PANI and vinyl group [62]. Note that these specific capacitance values were obtained from galvanostatic charge/discharge measurements carried out using a three-electrode system in 0.5 mol/L H₂SO₄ between 0 and 0.8 V [62]. A glassy carbon electrode with a diameter of 3 mm and loaded with 0.10 mg of the thin film of active material (containing one part (by mass) of PANI and 11 parts of 0.5 wt% Nafion [62][62][62][62][61][61][62][62][63][63][63][63]⁶³⁶³. Furthermore, ionic liquids doped PANI prevents the self-aggregation of PANI fibers, and thus facilitate the diffusion of the electrolyte ions into PANI-based electrodes [59, 62]. The improvement wettability of the IL-PANI electrode as compared with the conventional PANI seems to be logic, but it needs to be proven as apparent and dynamic contact angle measurements for the IL-PANI surface have not yet realized to the best of our knowledge.

6. Conclusion

Ionic liquids have been investigated as alternatives to the conventional aqueous acidic polymerization media (*e.g.*, HCl, H₂SO₄, *etc.*) to control PANI morphology, which largely impacts the electrochemical performances of PANI. It was reported that ionic liquids, like the conventional acidic media, are effective media to prepare PANI in emeraldine salt form. In contrast, ionic liquids have provided PANI with

new properties. Herein, the contribution of ionic liquids as polymerization media in controlling the morphology and properties of PANI is developed based on the most relevant studies. It was found that replacing the conventional polymerization media with the ionic liquids leads to:

- Decreasing the polymerization-rate.
- Improving the PANI solubility in organic solvents.
- Formation of nanostructured PANI morphology with controlled particles size instead of agglomerated morphology known for the conventional PANI.
- Improving the hydrophilicity of PANI as the ionic liquids can dope PANI through non-covalent interactions.
- Enhancing the electrochemical performances and electrochemical stability of PANI-based electrode materials for supercapacitors.

On the other extreme, the structure of the ionic liquids used as polymerization medium is a crucial parameter as it can impact not only the possible non-covalent interactions between PANI and the ionic liquids, but also the solubility of reaction mixture. As a result, the structure of ionic liquids affects the directing growth role of ionic liquids in the polymerization medium and its efficiency as a dopant for PANI. Finally, ionic liquids-doped PANI with nanostructures morphology exhibits better electrochemical performances and enhanced electrochemical stability, as compared with the conventional PANI. Thus, replacing the conventional media with ionic liquids seems to be a promising approach to obtain PANI with enhanced electrochemical stability. The challenge is to choose the ionic liquids which lead to the PANI formation with desirable properties as there are numerous available categories of ionic liquids with different choices of anions and cations. Choosing the type of ionic liquid, in which the PANI polymerization will be carried out, is crucial.

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