Electrochemical Synthesis of Polyaniline Zinc and Iron Oxide Composites and their Use in Energy Storage Applications

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Abstract: The fabrication of conducting polymers combined with metal oxides presents a promising avenue for the development of hybrid capacitive electrode materials. In this study, we employed a potentiostatic electrochemical polymerization method to in-situ synthesize integrated conductive polyaniline (PN) composites with various cheap and non-toxic metal oxides, including polyaniline zinc oxide (PNZ), polyaniline iron (III) oxide (PNF), and polyaniline zinc ferrite (PNZF). Thorough material characterization was conducted to gain insights into their morphological, structural, and compositional attributes. The synthesized hybrid electrode materials were then investigated for their energy storage capabilities using symmetrical supercapacitors in both two and three-electrode setups, employing cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS). Notably, the PNZF composite exhibited superior supercapacitive performance, attributed to its porous morphology and uniform distribution of $ZnFe_2O_4$ particles. The symmetrical supercapacitor constructed with PNZF demonstrated a high specific capacitance of 791.3 F g^{-1} at 1.0 A g^{-1}, and a power density of 1058.4 W kg^{-1}, an energy density of 136.4 Wh kg^{-1}, and excellent cyclic stability, retaining 86.1% of its initial capacitance after 4000 cycles. These findings underscore the suitability of PNZF as a hybrid electrode material for supercapacitor applications, based on its outstanding electrochemical performance. Our study offers valuable insights into the structural, optical, and electrochemical properties of PN composites, particularly PNZF.

Keywords: polyaniline; metal oxides; zinc ferrite; supercapacitor; electrochemical polymerization

1. Introduction

A sustainable energy transition requires clean and efficient conversion and storage of electrical energy using green energy resources like sun and wind. Addressing pressing concerns, it becomes crucial to explore diverse, clean, and sustainable energy sources [1]. In addition to energy storage devices, such as lithium-ion batteries, supercapacitors have attracted attention. Due to their inherent advantages such as fast charging and discharging rates, high power density, excellent thermal stability, and long service life [2], they have become widely used in various technologies, such as hybrid automobile vehicles, uninterruptable power supply, and electronic devices [3,4].

Current supercapacitors under development for energy storage include various electrode materials ranging from metal oxides and carbon compounds such as graphene and carbon nanotubes to conductive polymers and their composite blends [5-7]. Among polymer composites, typical electrode materials contain transition metal oxides such as MnO_2, Fe_2O_3, NiO, Co_2O_3, CdO, and ZnO, and conductive polymers like polyaniline (PN), polypyrrole, and polyindole [8-10].

PN has been widely used for energy storage and conversion due to its good optical, electrical, electrochemical, and thermal properties [11]. Due to the excellent material properties, polyindoles, particularly those incorporating transition metal oxides, are used in other technologies, too, such as fuel cells and photoelectrochemical water splitting – but the main application is in energy storage technologies.

For instance, using a chemical oxidative method, Gautam et al. synthesized PN-NiO composites (PN/NiO) by in-situ polymerization. The as-prepared hybrid electrode showed a specific capacitance of 623 F g^{-1} at 1 A g^{-1} current density with capacitance retention of 89% after 5000 cycles at a current density of 20 A g^{-1} [12]. Similarly, Kenesi et al. reported a ternary composite of PN and Cadmium oxide with graphene oxide (PN/CdO/GO), exhibiting a specific capacitance of 647 F g^{-1}, with a power and an energy density of 388 W kg^{-1} and 116.6 Wh kg^{-1}, respectively, and a capacitance retention of 82% after 500 cycles [13]. Further, it was reported the potentiodynamic in-situ polymerization of ternary PN composites with chromium and graphene oxide (PN/Cr/GO) that reached a specific capacitance of 243 F g^{-1} with a power density of 3.6 W Kg^{-1} and an energy density of 21.6 Wh Kg^{-1}, as well as a capacitance retention of 91% after 5000 cycles [14].

The studies support the use of hybrid electrode materials, combining various components to enhance the capacitive performance of polyaniline (PN). However, the current materials are costly due to expensive and often toxic metal oxides and the chosen synthesis method. In order to address these drawbacks, a direct synthesis of environmentally friendly and high-performance hybrid materials is required. Incorporating Fe_2O_3 with PN results in a redox-active composite with good capacitive performance, leveraging the multiple redox states of both components [15]. Despite these

advantages, challenges include significant volume expansion during the charge/discharge processes, causing mechanical stress and instability. The high magnetic nature of Fe_2O_3 leads to agglomeration over the PN matrix, decreasing surface area and practical capacitance [15]. To mitigate these issues, adding ZnO is proposed to enhance electrical conductivity. Binary metal oxides like zinc ferrite ($ZnFe_2O_4$) exhibit promising synergies with PN, offering improved capacitive performance and an extended lifespan [16].

Ghasemi et al. reported a ternary composite of PN with $ZnFe_2O_4$ and graphene oxide ($PN/ZnFe_2O_4/GO$) as hybrid electrode material synthesized by chemical oxidative polymerization. A specific capacitance of 594 F g^{-1} was achieved with an energy density of 45.2 Wh kg^{-1}, a power density of 302.7 W kg^{-1}, and 82% capacitance retention after 1500 cycles [17]. Similarly, another ternary composite of PN with $ZnFe_2O_4$ and reduced graphene oxide ($PN/ZnFe_2O_4/rGO$) using a chemical oxidative polymerization method achieved a specific capacitance of 1,419 F g^{-1} by 93% capacitance retention after 5000 cycles [18]. Integrating these metal oxides enhances the energy storage capabilities of polyanilines. Nevertheless, variations in specific capacitance, even with identical material synthesis and composition, underscore the incomplete understanding of the relationships between structure and performance.

Herein, we report on a direct electrochemical synthesis of PN composites with Fe_2O_3, ZnO, and $ZnFe_2O_4$ and their use as electrode materials in symmetrical supercapacitors. The active electrode material compositions and morphology were analyzed by SEM, EDX, UV-Vis and FTIR. The electrochemical properties of these composite electrodes were investigated via CV, GCD, and EIS measurements. The results indicate that $PN/ZnFe_2O_4$ nanocomposite electrodes possess the highest specific capacitance among the composites. The good electrochemical performance of the nanocomposites is attributed to the microporous structure that facilitates rapid ion diffusion and electrolyte penetration in these pores.

2. Materials and Methods

2.1 Chemicals

The following required chemicals were used for the synthesis of hybrid electrode materials: aniline monomer ($C_6H_5NH_2$, >99.5%), sulfuric acid (H_2SO_4, >98%), and dodecylbezenesulfonic acid (DBSA) ($C_{18}H_{30}SO_3$, >92%) were purchased from Merck (Kenilworth, NJ, USA), ferric chloride hexahydrate ($FeCl_3 \cdot 6\ H_2O$, >99%) and zinc chloride dihydrate ($ZnCl_2 \cdot 2\ H_2O$, >99%) from Sigma Aldrich (St. Louis, MO, USA) while, ammonia solution (NH_4OH; 33%) and *N*-methyl-2-pyrrolidone (NMP) were purchased from Across (Morris, NJ, USA). All chemicals received were of analytical grade and were used as received, except for aniline monomer, which was distilled twice before use. Double-deionized water was used for electrolyte preparation.

2.2 Material Characterisation

For morphological and elemental compositional analysis, scanning electron microscopy (SEM) coupled with energy-dispersive X-rays (EDX) spectroscopy was conducted using a field-emission scanning electron microscope (FESEM, JSM 5910 JEOL, Japan). X-ray diffractometry was employed using a diffractometer from Rigaku (Kyoto, Japan) with a Cu-Kα (λ = 1.54 Å) radiation with 2θ ranging from 10° to 80°, step width of 0.0164°, and a step rate of 1 s^{-1}.

Structural characterization of the synthesized polyaniline (PN) and its composites was carried out using a Fourier-transform infrared (FT-IR) spectrometer (IR-Affinity S1, Shimadzu, Kyoto, Japan) over a scanning range of 450–4000 cm^{-1}, with a resolution of 2 cm^{-1}. Additional analyses were performed using a UV-Vis spectrometer (UV-Vis Model 1800, Shimadzu, Japan) in the 200−1000 nm range.

2.3 Electrochemical Characterization

All electrochemical synthesis and analyses were conducted using a Reference 3000 potentiostat/galvanostat (Gamry Instruments, Warminster-PA, USA). Cyclic voltammetry (CV) measurements were executed in a three-electrode configuration using a gold sheet working electrode (1 cm^2) – either blank or polymer composite coated – and a gold rod counter electrode. As reference a saturated calomel electrode (SCE, KCl$_{sat}$ in H$_2$O). Galvanostatic charge-discharge (GCD) measurements were performed using the same three-electrode assembly. Specific capacitances were determined from CV and GCD curves for each sample using equations (1) and (2) respectively [19].

$$C_S = \int \frac{I \cdot dv}{2m \cdot v \cdot \Delta V} \qquad (1)$$

$$C_S = \frac{I \cdot t}{m \cdot V} \qquad (2)$$

Here, $\int I\,dv$ is the integrated charge of the CV curve (C), m is the mass (g) of the active material, v is the scan rate (mV s^{-1}), ΔV is the potential window (V), t is the discharge time (s), and V is the IR-drop corrected potential (V).

Additionally, energy density (Wh kg^{-1}), power density (W kg^{-1}), and columbic efficiency η (%) were calculated from equations (3), (4) and (5) respectively [9,20,21].

$$E = \frac{C_S \cdot (\Delta V)^2}{2} \qquad (3)$$

$$P = \frac{3600 \cdot E}{t} \qquad (4)$$

$$\eta(\%) = \frac{t_d}{t_c} \cdot 100 \qquad\qquad (5)$$

Here, t_d and t_c are discharge and charge times in seconds (s).

Furthermore, electrochemical impedance spectroscopy (EIS) was employed to investigate charge transfer resistance (R_{CT}) at the electrode/electrolyte interface, ions diffusion, and internal resistance (R_S). During EIS measurements, the excitation amplitude was fixed at 5 mV$_{rms}$, within the frequency range of 10^5 Hz to 10 mHz and at open circuit.

2.4 Synthesis of metal oxide nanoparticles

The synthesis of different metal oxide nanoparticles was carried out by the co-precipitation method [22]. For the synthesis of ZnO and Fe_2O_3, $ZnCl_2 \cdot 2H_2O$ (1.36 g, 10.0 mmol, 1.0 eq) and $FeCl_3 \cdot 6H_2O$ (2.70 g, 9.98 mmol, 1.0 eq) were dissolved in 100 mL distilled water, respectively, and stirred at 80 °C for 30 min. The mixture was filtered, and ammonia solution (33%) was added dropwise until a pH of 10 was set. The nanoparticles precipitated as their respective hydroxides. They were filtered, washed with distilled water and ethanol, and dried at 120 °C for 20 min. Then, they were calcined at 600 °C for 2 hours with a heating rate of 10 °C /min to obtain ZnO and Fe_2O_3 nanoparticles, respectively.

The same procedure was used to synthesize $ZnFe_2O_4$ nanoparticles using ZnO and Fe_2O_3 together in a 1:2 eq. ratio. All nanoparticles were characterized by XRD.

2.5 Potentiostatic Electro-deposition of PN and PN/Composites

For the synthesis of the PN composites, a multistep synthesis sequence was used. An aniline precursor solution was prepared by dispersing aniline (1.0 mL, 10.9 mmol, 1.0 eq) in distilled water. Then H_2SO_4 (5.55 mL, 1M) and DBSA (0.5 mL, 2.2 mmol, 2.01 eq) were added. The solution was thoroughly mixed, and distilled water was added to a total volume of 100mL [23,24]. In the case of the PN composite synthesis additionally the metal oxides (0.1 g) were added to the solution.

Electrolytic deposition of PN and its metal oxide composites was carried out using chronoamperometry in a three-electrode setup. Suitable potentials for polymerization and incorporation of the Zn and Fe oxide nanoparticles were determined by linear and cyclic voltammetry. Using a gold working electrode at 0.8 V vs. SCE for 600 s, a thin PN film was deposited slowly at the electrode. Then a negative potential was then applied to achieve ion exchange with the Zn and Fe oxide nanoparticles [25]. For example, a potential of 0.6 V was applied vs. SCE to deposit ZnO nanoparticles over 600 s to yield the PN@ZnO composite (PNZ).

Similarly, for the deposition of Fe_2O_3 and $ZnFe_2O_4$ particles, -0.7 V and -0.9 V were applied for 600 s to obtain $PN@Fe_2O_3$ (PNF) and $PN@ZnFe_2O_4$ (PNFZ). The electrodeposition process was repeated three times to obtain a fully covered electrode. Alternatively, the same results were obtained, using cyclic voltammetry for the electro-deposition. Thereby, it was cycled in the respective potential range for 5 cycles with a scan rate of 50 mV s^{-1}. The composites were thoroughly washed with distilled water and acetone afterward and dried in all syntheses.

3. Results and Discussion

3.1 Identification of Potentials for the Potentiostatic Electrodeposition

The key to uniform electrochemical polymerization at electrodes is identifying suitable reaction conditions, mainly controlling the operating potential. The potential must be high enough to initiate polymerization on the electrode but not too high to trigger overoxidation or the formation of secondary degradation products [26,27]. The electrochemical synthesis of PN and its composites is particularly elegant, as the oxidation potential can be finely adjusted, and the reaction can be switched off directly after a defined time. This is challinging to achieve with chemical oxidation.

Either linear sweep voltammetry or cyclic voltammetry was used to identify a suitable oxidation potential for both PN electro-deposition and reductive deposition of the nanoparticles in the polymer (Figure 1).

Figure 1a shows an aniline solution's linear sweep voltammogram (LSV) between 0 and +1.0 V vs SCE. Aniline polymerizes from a potential of +0.8 V vs SCE. Between +0.8 V and +0.9 V, only aniline is oxidized. The electrolyte solution decomposes at potentials greater than +0.9 V, and further overoxidation occurs. We have therefore decided on a potential of +0.8 V for PN synthesis, as in other reports on PN electro-polymerization [27].

The potential range for metal oxide deposition on the PN-coated electrodes was determined similarly. The potential range for metal oxide deposition on the PN-coated electrodes was determined the same way. LSV was measured in the potential range between 0 and -1.0 V against SCE with a scan rate of 50 mV s^{-1}. Suitable potentials for the deposition of ZnO, Fe_2O_3, and $ZnFe_2O_4$ are -0.6 V, -0.7 V and -0.9 V respectively (see Figure 1b).

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Figure 1. (a) Linear sweep voltammetry (LSV) of aniline, and (b) cyclic voltammetry of ZnO, Fe_2O_3 and $ZnFe_2O_4$ in the synthesis precursor solution.

3.2 Electrochemical Synthesis of the Polyaniline Composites

During all PN syntheses, the chrono-amperograms show a dynamic non-linear behavior (Figure 2). Initially, a rapid increase in current density was observed for pure PN, lasting about 50 s. The rapid initial increase in current density can be attributed to the fast reaction kinetics of the polymerization of multiple polymer chains [28]. The increase was followed by a decrease in current density over approximately 170 s due to the growth of longer polymer chains and fast consumption of aniline in the diffusion layer, leading to a mass transport limitation. With an increase in the chain length, the polymerization's reaction kinetics decrease leading preventing mass transport limitation, resulting in a steady increase in current density until the end of the polymerization [29]. A similar trend was observed during the PN polymerisation in the presence of ZnO, Fe_2O_3, and $ZnFe_2O_4$ metal oxide particles [30,31].

3.3 Physico-chemical Characterisation of the Polyaniline Composites

The physical and chemical properties of pristine polyaniline (PN) and its composites PNZ, PNF, and PNFZ, are discussed in the following. In supercapacitors, the capacitive properties of an electrode material are intricately linked to its structural characteristics and surface area. Thus, attaining high electrochemical performance necessitates a nanostructured morphology that

maximizes surface area and provides unobstructed pathways for efficient ion transport. To 210
understand the impact of composite synthesis on material structure, SEM images were recorded for 211
all compounds. Figure 3 illustrates the morphological features of PN, PNZ, PNF, and PNFZ, 212
providing insights into the structural features and differences. 213

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Figure 2. Current-time response (I-t) profiles during synthesis of (a) PN, (b) PNZ, (c) PNF, and (d) 215
PNZF 216

From the SEM images shown in Figure 3, it is evident that each polymer sample exhibits a 217
heterogenous and porous surface morphology. PN possesses irregular agglomerated short fibrous 218
growth patterns (Figure 3a). The strands length is ~1 μm on average, and the width is between 300- 219
500 nm. The interwoven strands form small voids of similar size. PNZ and PNF exhibit a much 220
denser microstructure, which consists of several micrometer-sized particles that are strongly 221
agglomerated (Figure 3b and c). Particularly noticeable for PNF is the pronounced agglomeration 222
of the composite, which can be attributed to the magnetic properties of the Fe_2O_3 nanoparticles 223
incorporated in the polymer structure [32]. 224

In contrast to the other composites, PNZF shows short fibrous growth patterns, with strand 225
lengths of ~1-3 μm on average and strand widths between 250-300 nm (Figure 3d). The surface is 226
rougher with small nanoparticles on it: $ZnFeO_4$. Further large voids of 1 to 3 μm diameter are visible. 227
The open structure of PNZF supports the hypothesis that Zn counteracts the agglomeration effect 228
of the iron oxide, as reported in [33]. 229

Figure 3. SEM images of (a) PN, (b) PNZ, (c) PNF, and (d) PNZF.

Nevertheless, the PNFZ composite synthesized by Patil et al., using a chemical oxidative method with 10 wt. % zinc ferrite produced similar particles but in larger sizes, approximately ~600 nm [34]. In contrast, our method demonstrates the production of PNFZ with a larger surface area and higher porosity, validating the viability of direct electrochemical synthesis for PNFZ composites.

Structural features of PN and its composites with metal oxides were analyzed using X-ray diffraction (XRD), as shown in Figure 4. The XRD pattern of PN synthesized by cyclic voltammetry and chronoamperometry (Figure 4a and 4b) exhibited a single broad band at 2θ = 25.9° and 32.1°, indicating its highly amorphous nature. The XRD pattern of ZnO and PNZ showed characteristic peaks at 2θ = 32.1°, 34.7°, 37.1°, 47.3°, 57.7°, and 67.9°, consistent with previously reported values (Figure 4c and d) [25]. The XRD pattern of Fe_2O_3 exhibited characteristic peaks at 2θ = 24.2°, 34.0°, 35.6°, 42.0°, 49.7°, 54.2°, 57.6°, 62.9°, and 64.1°, indicating its crystalline nature without any impurities (Figure 4e and f) [35,36]. The diffraction peaks of zinc ferrite and PNZF (Figure 4g and 4h) were observed at positions 2θ = 18.2°, 30.1°, 35.41°, 43.1°, 53.2°, 56.3° and 65.2°, consistent with the spinel cubic phase due to the presence of hexagonal ZnO and Fe_2O_3, forming the bimetallic $ZnFe_2O_4$ [37] . The absence of extra peaks confirmed the absence of impurities during the synthesis of metal oxides and PN composites. The average crystallite size (D) was calculated using Scherer's formula (eq. 6) [37]:

$$D = (K \cdot \lambda)/(\beta \cdot \cos\theta) \qquad (6)$$

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Here is K = 0.9 (Scherer constant), λ = 0.15406 nm (wavelength of X-rays), β = full width at half maximum (FWHM) in radians, and θ is the peak position on the x-axis.

The peak position and FWHM from XRD data were used to calculate the average crystallite size for $ZnFe_2O_4$, PNZF, Fe_2O_3, PNF, ZnO, and PNZ, which were found to be 21.51 nm, 25.34 nm, 29.42 nm, 27.2 nm, 33.19 nm, and 24.7 nm, respectively.

Figure 4. XRD spectra of (a) PN synthesized by CV during parameter identification, (b) PN synthesized by CA, (c) ZnO, (d) PNZ, (e) Fe_2O_3, (f) PNF, (g) $ZnFe_2O_4$, (h) PNZF.

The chemical structure and functional groups of metal oxides, PN, and its composites were investigated by FTIR analyses. The FTIR spectra of pure PN and its composites show clear characteristic peaks (Table 1). For example, the peak at 3260 cm^{-1} corresponds to the N-H bond stretching vibrations in the PN polymer chain (Figure 5a) [38]. In addition, a notable and relatively intense peak at 1530 cm^{-1} indicates the C=C stretching of the benzoid ring. The persistence of this peak in the composites confirms the polymer composition's retention after the composites' formation. The EDX pattern shown in Figure S2 also confirms that the electrochemical incorporation of various metal oxide particles into the polymers does not affect the polymer composition [39]. The appearance of a peak at 1490 cm^{-1} indicates a C-N stretching vibration. Compared to pure PN, this peak is more pronounced in the composites, indicating the binding of the metal oxides to the nitrogen in the polymer chain. The characteristic bands in the 1142-1154 cm^{-1} range are assigned to the C-H bending vibration in the plane of the aromatic benzoid/quinoid rings, which also explains the

delocalization of the pi electrons [40]. In conclusion, the bands shown by PN are preserved in the composites, indicating that metal oxides are efficiently.

The FTIR spectra of the metal oxides (see Figure 5b) explain the structural features of the corresponding metal oxides. The bands at 720, 950, and 1060 cm^{-1} can be assigned to ZnO, Fe_2O_3, and $ZnFe_2O_4$, respectively. A broad band at 3500 cm^{-1}, present in the FTIR spectra of all metal oxides, is due to OH stretching. This band illustrates the porous nature of the metal oxides, which contain moisture in the pores of the metal oxides [41]. This peak is more pronounced and broader in the spectrum of ZnO, indicating a higher water content than other metal oxides. To summarize, the FTIR spectra of metal oxides differ overall from those of PN and PN composites.

Figure 5. FT-IR spectra of (a) PN and its composites, (b) ZnO, Fe_2O_3 and $ZnFe_2O_4$.

Optical characterization of metal oxides, PN, and the PN composites was done to gain insights into their doping level and charge transport during electronic excitation. Therefore, all the samples were dissolved in appropriate amounts of NMP, and UV-vis spectra were recorded in the range of 200-800 nm. The obtained spectra for metal oxides and PN composites are shown in Figure 6a and Figure 6b, respectively.

Table 1 Position of FTIR vibrations observed for the PN and PN composites.

PN (cm^{-1})	PNZ (cm^{-1})	PNF (cm^{-1})	PNZF (cm^{-1})	Peak assignments
1105	1134	1138	1153	CH bending
1303	1308	1307	1370	-N=Quinoid=N-
1402	1402	1403	1405	CN bending
1570	1570	1571	1579	CN stretching
1581	1577	1574	1580	Benzenic quinoinic nitrogen
1608	1609	1610	1619	C=C stretching

The UV-vis spectra of PN and PN composites reveal three characteristic peaks. The first peak in the range of 720-800 nm is attributed to the creation of excitons that cause the bipolaron transition [42]. The bipolaron transition in PNZF was observed at 750 nm, while for PNZ and PNF, it was observed at 680 nm and 800 nm, respectively. The second peak in the range of 380-430 nm represents the polaron transition of quinoid rings present in PN as well as in composites [43]. The relatively higher intensity absorbance peaks observed in the range of 280-300 nm represent the π-π* transition of the aromatic/benzoid rings of composites and pure PN [44]. Specifically, for PNZF, this peak was observed at 280 nm, while for PNF and PNZ, it was observed at 300 nm and 290 nm, respectively.

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Figure 6. UV/Vis spectra of (a) PN and its composites and (b) ZnO, Fe$_2$O$_3$, and ZnFe$_2$O$_4$.

On the other hand, the UV-Vis spectra of metal oxides showed a single and characteristic absorption peak in the range of 270-320 nm. The absence of extra peaks implies the purity and well-crystalline nature of the metal oxides [45]. This single prominent and characteristic absorption peak was observed at 270 nm for ZnO, 320 nm for Fe_2O_3, and at 380 nm for $ZnFe_2O_4$ [46]. The shifting of peak position is related to bathochromic shift, which was a reason for selecting bimetal oxides to synthesize an imminent composite electrode material for future supercapacitors.

3.3 Electrochemical Characterisation of the Polyanline Composites

To validate that the PN composites are suitable as electrode material for supercapacitors, the electrochemical properties were investigated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS).

Since the cyclic voltammetry of PANI composites has already been described in detail in the literature, only the general behavior is presented here. Figure 7 shows the CVs of PN, PNZ, PNF, and PNFZ between potentials of $\square$0.2 V and 0.9 V (vs. SCE, KCl$_{sat.}$ in H_2O) with different scan rates. All electrochemical measurements were carried out in 1M H_2SO_4 solution. Figure 7a depicts the cyclic voltammogram of polyaniline (PN), revealing three distinct redox transitions. The first two reversible transitions occurring at potentials of $\square$0.06 V to 0.15 V and 0.33 V to 0.43 V are characteristic of PN and correspond to the conversion from leucoemeraldine to emeraldine, and subsequently to pernigraniline. These transitions describe the oxidation and reduction processes required to convert PN between its different oxidation states.

Figure 7. Cyclic voltammograms of (a) PN, (b) PNZ, (c) PNF, and (d) PNFZ at different scan rates. Potentials are referred to SCE (KCl$_{sat.}$ in H_2O).

The third redox transition observed can be attributed to smaller polymer chains undergoing additional chain growth, ion doping/de-doping processes, or proton addition/removal. As a result, this transition exhibits irreversible redox behavior, indicating complex molecular interactions and structural transformations within the PN matrix. For PNZ, PNF, and PNZF, analogous electrochemical behaviors were observed in the CVs (Figure 7b-d). These composites also display three distinct redox transitions clearly visible at low scan rates. However, at higher scan rates, the peaks merge due to the increased current, resulting in near-rectangular CV shapes attributed to the heightened double-layer capacitance. Furthermore, an upward shift in the potential of the redox peaks at faster scan rates suggests hindered charge transfer processes.

When comparing the cyclic voltammograms (CVs) of polyaniline (PN) and its composites, it is evident that PNFZ has the highest redox activity (Figure 8a). The electrochemical charge storage capability was compared for each material by determining its specific capacitances from the cyclic voltammograms. The highest specific capacitance of 870 F g^{-1} was obtained for PNZF at a scan rate of 5 mV s^{-1}. For PNF, PNZ, and PN lower specific capacitances of 485, 320 and 317 F g^{-1} were obtained, respectively. Thus, incorporating ZnFe$_2$O$_4$ resulted in a significant increase in charge storage capability compared to the other electrode materials. As the scan rate increases, all composites' specific capacitances drop steadily. This trend occurs due to the slow mass transport of electrolyte ions inside the porous active material. Consequently, the charge storage capability is lower (Figure 8b).

Figure 8. Comparison of PN and its composites for (a) CV measurements at a scan rate of 5 mV s^{-1}, (b) the calculated specific capacitances of PN, PNZ, PNF and PNZF for different scan rates, (c) the calculated capacitance retentions for 4,000 cycles at 30 mV s^{-1}.

To further investigate the charge storage mechanism occurring at the electrode-electrolyte interface, the current dependence on scan rate was analyzed using equation (2) [9,10].

$$\log I = \log a + b \log v \qquad (7)$$

In this equation, *b* represents the slope is directly associated with the charge storage mechanism. For instance, a value of "b" equal to 0.5 suggests a diffusion-controlled process, while a value higher than 0.5 indicates a surface-controlled process. Among the different electrode materials investigated, PNZF exhibited the highest values: 0.84 for oxidation and 0.71 for reduction (Figure S2). This suggests a predominantly surface-controlled process. However, the impact of mass transport by ion diffusion is still contributing to the overall performance at high scan rates [9].

Moreover, the cycle stability of PN and its composites was investigated at a scan rate of 30 mV s^{-1} for 4000 consecutive CV cycles within the potential range of 0 to 1.1 V. As illustrated in Figure 8c, all four polymers exhibit a linear decrease in capacitance retention over the entire cycling duration. PN and PNZ demonstrate comparable and relatively low cycle stability, dropping below 70% capacitance retention after 4000 cycles. Similarly, PNF follows a comparable trend with a capacitance retention of approximately 80% over the cycling experiment. Notably, the highest capacitance retention is observed for PNFZ, reaching 90% throughout the entire testing period. The linear decrease in capacitance retention suggests the presence of a consistent degradation mechanism persisting throughout the cycle test, with no additional processes occurring in the later stages that alter the rate of performance loss.

Figure 9 shows the GCD profiles of PN and its composites at different current densities between 0.5 F g^{-1} to 10 F g^{-1}. The asymmetric and distorted triangular shape in the potential range from 0 V to 1.1 V originates from the pseudocapacitive behavior of the materials. It is especially dominant for PNF and PNZF, thus underscoring their high pseudocapacitive nature compared to PN and PNZ samples (Figure 9a-d). Notably, the charge-discharge duration of PNZF surpassed that of the other samples, suggesting the positive contribution of $ZnFe_2O_4$ doping to the polymer structure. The synergistic interaction between the $ZnFe_2O_4$-dopant and the polymer network resulted in an increase in electrical double-layer capacitance, additionally to the pseudo-capacitance stemming from redox reactions at the electrode interface.

Furthermore, in the case of PN, PNZ, and PNF, a noticeable instantaneous voltage drop occurs when the supercapacitor changes from charging to discharging. This drop results from the cumulative ohmic resistance of the electrodes, electrolyte, and contact resistances within the electrode structure. Consequently, the total usable voltage window (ΔV) is reduced by the IR drop, contributing to the lower charging and discharging times of these three materials. For PNFZ the IR drop is significantly lower, thus the charge and discharge time higher.

Consequently, the comparison reveals significantly lower specific capacitances for PN, PNZ, and PNF of 476, 280, and 182 F g^{-1}, respectively, at a current density of 1 A g^{-1}. In contrast, PNFZ exhibits the highest specific capacitance of 791 F g^{-1} at the same current density. These findings

are consistent with those obtained from the CV analysis. Moreover, the decrease in specific capacitances with increasing current densities across the various electrodes suggests that the processes are predominantly surface-controlled and exhibit only mass transport limitations at high current densities, as indicated by the CV results [47].

Figure 9. GCD experiments at different current densities of (a) PN, (b) PNZ, (c) PNF, and (d) PNZF. (e) Comparison of the specific capacitances of PN and its composites at different current densities.

A comparison of various polyaniline composite electrode materials in three-electrode setup is presented in Table 2. The analysis of PNFZ reveals comparable charge storage capabilities to those incorporating cobalt-iron oxide and nickel-iron oxides, however, it stands out due to its non-toxic dopant. Consistent with PN composites, PNFZ exhibits a notably high power density of 1058.4 W kg^{-1} alongside a moderate energy density of 136.4 Wh kg^{-1} at 1 A g^{-1}, making it suitable for high power applications.

Table 2. Comparison of various PN/metal oxides electrodes for supercapacitors.

Electrode	Method of synthesis	Capacitance (F g^{-1}) at 1 A g^{-1}	Energy density (Wh kg^{-1})	Power density (W kg^{-1})	Capacitance retention (%)	References
PN/GO/ZnFe$_2$O$_4$	Hydrothermal	594	45.2	302.7	82	[17]
PN/Fe$_2$O$_3$/rGO	Chemical oxidative polymerization	283.4	47.4	550	78	[48]
PN@Fe-Ni co-doped Co$_3$O$_4$	In-situ oxidative polymerization	1171	144	-----	84	[49]
PN/NiFe$_2$O$_4$/rGO	In-situ oxidative polymerization	1134.2	19.3	610	76.5	[47]
PN/CoFe$_2$O$_4$/GO	Chemical oxidative polymerization	1123	240	2680	98.2	[50]
PNZF	Potentiostatic electrochemical polymerization	791.3	136.4	1058.4	86.1	this work

3.3.4 Analysis of PN and its Composites in a Symmetrical Supercapacitor

For realistic performance analysis of PN, PNZ, PNF and PNFZ, they were assembled in a symmetrical supercapacitor and investigated by GCD and EIS in a two-electrode setup. The symmetrical setup results in similarly shaped charge-discharge curves that became more rectangular. Their specific capacitances were calculated from the discharge curves measured at 1 A g^{-1} and the respective energy and power density and coulombic efficiency were determined (Table 3).

PN exhibits moderate charge storage capabilities with a specific capacitance of 181.3 F g^{-1}. It demonstrates a relatively high power density at 1058.4 W kg^{-1}, albeit with a moderate energy density of 31.3 Wh kg^{-1}. Despite this, PN maintains a high Coulombic efficiency of 130.31%. In contrast, PNZ exhibits slightly improved charge storage properties with a higher specific capacitance of 280.6 F g^{-1}. However, its power and energy density are comparatively lower at 774.0 W kg^{-1} and 25.9 Wh kg^{-1}, respectively. The low specific capacitance for PNZ contradicts the results from the three-electrode measurements. The negative polarization of the respective counter electrode in the two-electrode setup may cause losses during the GCD cycles, leading to performance loss.

Additionally, like for PN, for PNZ, a coulombic efficiency of 123.9% was observed. The coulombic efficiency higher than 100% indicates that an irreversible process is taking place during

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the GCD experiment. This is consistent with the cycle stability experiments with three electrodes, in which PN and PNZ showed the lowest capacity retention over 4,000 cycles and, thus, the fastest degradation.

In contrast, PNF demonstrates superior charge storage capabilities compared to PN and PNZ, with a significantly higher specific capacitance of 475.9 F g^{-1} and a good energy and power density, with values of 65.1 Wh kg^{-1} and 941.4 W kg^{-1}, respectively. PNF maintains a high Coulombic efficiency of 90.5%. Amongst the different samples, PNZF stands out again with the notably highest specific capacitance of 791.3 F g^{-1}. The energy and power density, therefore, were 136.4 Wh kg^{-1} and 1058.4 W kg^{-1} respectively and a coulombic efficiency of 82.2%. The decrease in coulombic efficiency arises from a prolonged duration for the complete charge-discharge sequence. However, the results show that the doping of PN with $ZnFe_2O_4$ leads to exceptionally good performance and energy storage properties suitable for high power applications.

Table 3. Specific capacitances, energy densities, power densities, and coulombic efficiencies for PN and its composites at 1 A g^{-1}.

Sample	Charge time (s)	Discharge time (s)	Discharge potential (V)	Specific capacitance (F g^{-1})	Energy density (Wh kg^{-1})	Power density (W kg^{-1})	Coulombic efficiency (η %)
PN	106.6	81.8	0.59	181.3	31.3	1058.4	130.3
PNZ	120.7	97.4	0.43	280.6	25.9	774.0	123.9
PNF	248.9	275.1	0.52	475.9	65.1	941.4	90.5
PNZF	464.1	564.6	0.59	791.3	136.4	1058.4	82.2

The performance of electrochemical devices involves analyzing various types of losses, including charge transport losses, charge transfer losses due to electrochemical reactions, and losses attributed to reactant diffusion. Electrochemical impedance spectroscopy enables the characterization of these processes individually by separating them by their respective time constants, thus showing their individual contributions to the total loss. Figure 10 illustrates the Nyquist plots obtained from measurements conducted on PN and PN composite-coated electrodes at OCP.

The spectra can be divided into three distinct regions: (1) the high-frequency region (> 1 kHz) is attributed to the bulk resistance, comprising the charge transport resistance stemming from the current collector, wiring, and both electrical and ionic transport through the electrode and electrolyte; (2) a broad and open semi-circle observed in the mid-frequency range (1 kHz to 5 Hz), attributed to the electrode interfaces' double layers and charge transfer processes; [51,52] and (3) a

monotonically increasing slope observed at frequencies below 5 Hz to 0.1 Hz, typically associated with ion diffusion within the active material and other slower diffusion processes [53].

Through this analysis, the intricate interplay between these fundamental processes can be identified, providing valuable insights into the loss mechanisms that determine the electrochemical performance of supercapacitors.

The analysis of EIS parameters was done, using a simplified electrical equivalent circuit (EEC). This EEC comprises several elements: a bulk resistance (R_{Bulk}) in series with a polarization resistance (R_{pol}) that is in parallel arrangement with a constant phase element (CPE) to characterize the electrical double layer, and in series a charge transfer resistance (R_{CT}) in parallel with another CPE element to fit the pseudocapacitive part of charge transfer, and an open Warburg element (Wo) to model ion transport within the polymer particles.

Figure 10. EIS spectra of PN, PNZ, PNF, and PNFZ. The EEC for fitting the spectra is shown below.

For all four electrode materials, low bulk resistances ranging from 0.50 Ω to 1.11 Ω were observed, underscoring the high conductivity of both the electrode material and the remaining components of the supercapacitor. In the case of PN and PNZ, notably high polarization resistances of 130.6 Ω and 74.0 Ω were obtained, likely stemming from irreversible loss processes at the electrode/electrolyte interface, contributing to their lower Coulombic efficiency. Conversely, PNF and PNFZ exhibited lower polarization resistances of 6.45 Ω and 34.7 Ω, respectively.

Furthermore, high charge transfer resistances were observed for PN (109.4 Ω), while PNZ and PNF showed intermediate values of 44.2 Ω and 51.5 Ω, respectively. This indicates kinetic limitations during the electrochemical redox reaction of the polymer for these three cases. In contrast, PNFZ demonstrated a significantly lower charge transfer resistance of 25.0 Ω, suggesting higher efficiency in charge transfer and thereby translating into superior charge storage capability [54]. Additionally, at the low-frequency range, an almost ideal Warburg diffusion behavior was observed across all cases. This finding suggests minimal mass transport influence attributed to slow ion diffusion, indicating a predominantly surface-controlled charge storage mechanism for all materials.

These insights highlight the intricate interplay between different resistance components and their impact on the electrochemical performance of the supercapacitor electrodes.

4. Conclusions

Herein, we present a comprehensive investigation into the in-situ synthesis and performance analysis of polyaniline (PN) composites with ZnO (PNZ), Fe_2O_3 (PNF), and $ZnFe_2O_4$ (PNFZ) dopants as electrode materials for symmetrical supercapacitors. Through SEM, EDX, FTIR, and UV-Vis analyses, we characterized the composition and morphology of the active electrode materials. Furthermore, the electrochemical properties of these composite electrodes were extensively evaluated using cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy. The combination of material analysis and electrochemical characterization enabled us to establish a direct correlation between electrode structure and charge storage properties.

SEM images illustrate the heterogeneous and porous surface morphologies of the polymer samples, with PN showing irregular agglomerated short fibrous growth patterns. In contrast, PNZ and PNF exhibit denser microstructures composed of strongly agglomerated particles. Notably, PNFZ displays short fibrous growth patterns with a rougher surface, indicating the synergistic effects of zinc and iron oxide doping. XRD analysis confirms the amorphous nature of PN and the crystalline nature of the metal oxides and composites. The average crystallite sizes vary across the materials, reflecting differences in their structural properties. FTIR and UV-Vis spectra show characteristic features corresponding to the functional groups present in the polymer and metal oxides. The

retention of these peaks in the composites confirms the efficient incorporation of the metal oxides into the polymer matrix.

In electrochemical characterization, CVs exhibit distinct redox transitions corresponding to the conversion between different oxidation states of PN and its composites. Incorporating of $ZnFe_2O_4$ significantly enhances the charge storage capability compared to other electrode materials. Analysis of charge-discharge profiles in two- and three-electrode setups and quantification of their respective specific capacitances further confirms the superior performance of PNFZ with 791.3 F g^{-1} at a discharge current density of 1 A g^{-1}, attributed to its high pseudocapacitive nature and efficient charge transfer processes. The respective energy and power densities were 136.4 Wh kg^{-1} and 1058.4 W kg^{-1}, making PNFZ an suitable electrode material for high power charge storage applications. EIS measurements reveal the intricate interplay between different resistance components, highlighting a surface-controlled charge storage mechanism prevalent in all materials. Furthermore, PNFZ showed the highest capacitance rention of ~90% over 4,000 cycles.

Overall, our study demonstrates the promising potential of PN composites, particularly PNFZ, as electrode materials for high-performance supercapacitors, offering insights into their structural, optical, and electrochemical properties for future energy storage applications.

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