Electrochemical Polymerization of Polyaniline: A Comprehensive Review of Synthesis Conditions, Nanocomposites, and Industrial Applications

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Abstract

The increasing demand for conductive polymers, particularly polyaniline (PANI), has been driven by their versatility and unique electrical, optical, and mechanical properties, making them highly valuable in applications such as energy storage, corrosion protection, flexible electronics, sensors, and biomedical devices. Market projections indicate a robust growth trajectory, with a compound annual growth rate of 7.3% from 2024 to 2030, culminating in an estimated market value of USD 8.6 billion. Despite its advantages, traditional chemical polymerization methods for PANI synthesis often involve the use of toxic reagents, generate hazardous by-products, and require complex purification steps. As a result, electrochemical polymerization has emerged as a sustainable and efficient alternative, offering precise control over polymer morphology, doping levels, and conductivity while minimizing environmental impact.

This review systematically examines the key parameters governing the electrochemical polymerization of PANI, including electrode material composition (e.g., platinum, carbon-based, and metal oxides), electrolyte solution types (acidic, neutral, or ionic liquid-based media), choice of dopant acids (e.g., HCl, H_2SO_4, p-toluenesulfonic acid), applied electric potential (galvanostatic vs. potentiostatic conditions), polymerization duration, and temperature effects. Each of these factors significantly influences the structural, mechanical, and electrical properties of PANI, impacting its performance in specific industrial applications. Furthermore, the correlation between synthesis conditions and key functional attributes such as electrical conductivity, charge storage capacity, chemical stability, and adhesion properties is critically analyzed.

Special emphasis is placed on optimizing electrochemical polymerization techniques for application-specific requirements, such as enhancing charge transport mechanisms for supercapacitors, improving biocompatibility for medical sensors, and increasing adhesion for anti-corrosion coatings. Additionally, this review highlights recent advances in nanostructured PANI composites, hybrid materials, and scalable fabrication techniques that address challenges related to industrial-scale production. By integrating fundamental principles with emerging research trends, this study aims to provide a comprehensive roadmap for optimizing PANI synthesis, ultimately enabling its broader adoption in next-generation technologies.

Introduction And Background

Conductive polymers have garnered significant attention due to their unique ability to transition reversibly between different oxidation states, exhibiting variable electrical conductivity and color change [1]. Among the various classes of conducting polymers, polyaniline (PANI), polypyrrole (PPy), and polythiophene (PT) have emerged as particularly valuable materials owing to their excellent corrosion resistance, lightweight nature, and ease of synthesis [2-4]. These polymers provide an effective immobilization platform, facilitating electron transport and enabling efficient signal transduction in various applications [5].

PANI is of particular interest due to its ability to undergo reversible redox transformations, which allow for controlled modulation of its electrical properties through protonation or oxidation-state adjustments. Its exceptional electrical conductivity, cost-effectiveness, mechanical flexibility, and remarkable chemical

and thermal stability make it a versatile material for a wide range of applications, including electronics, optics, and microelectronics. PANI has been extensively utilized in the development of membranes, pigments, and flame retardants. Furthermore, its high conductivity, large surface area, and reversible charge storage capacity have made it an attractive candidate for sensors, biosensors, and energy storage devices. Figure *1* illustrates the diverse applications of PANI and its nanocomposites.

Various conventional physical and chemical techniques have also been applied efficiently to synthesize PANI [6-8]. Electrochemical polymerization (EP) has demonstrated significant advantages over conventional chemical oxidative polymerization methods among the various synthesis techniques for conductive polymers. PANI synthesized via electrochemical routes exhibits enhanced chemical and electrochemical stability, which substantially influences its morphological structure, conductivity, doping efficiency, optical properties, and overall performance. The EP process offers multiple benefits, such as the ability to control film geometry through electrode configuration, direct deposition onto conductive or non-conductive substrates, solvent- and catalyst-free synthesis, higher purity and reproducibility, and superior environmental compatibility. Additionally, the controlled deposition process allows for the fabrication of highly defined surface patterns, making EP a preferred method for PANI synthesis in various technological applications [9].

To further enhance the properties of PANI, researchers have explored the incorporation of metal and carbon-based nanoparticles, leading to the development of PANI nanocomposites. These hybrid materials combine the advantageous characteristics of both PANI and nanomaterials, resulting in improved conductivity, mechanical strength, and functional performance. Metal nanoparticles (e.g., silver, gold, copper, and palladium) and carbon nanostructures (e.g., graphene oxide and carbon nanotubes) have been successfully integrated with PANI, leading to synergistic effects that enhance the overall material properties [10].

This review aims to provide a comprehensive analysis of the electrochemical polymerization of polyaniline and its nanocomposites. It examines various synthesis techniques, compares electrochemical methods with other polymerization approaches, and discusses the effects of synthesis parameters on the structural, electrical, and morphological properties of PANI. Additionally, this study highlights key applications of PANI and its nanocomposites across diverse industrial sectors, offering insights into their future potential and emerging research directions.
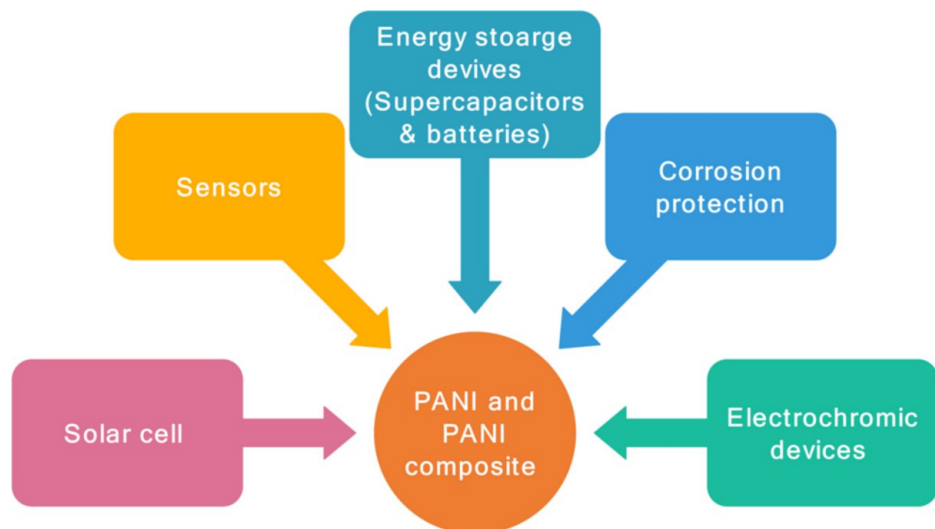
FIGURE 1: Applications of PANI and PANI composites in different sectors

PANI, polyaniline

Review

Electrochemical polymerization of polyaniline

Electrochemical polymerization is a widely adopted technique for the synthesis of PANI due to its ability to control polymer growth and structural properties with high precision. Compared to chemical oxidative polymerization, electrochemical methods offer several advantages, including the ability to tailor film thickness, morphology, and doping levels by adjusting electrochemical parameters. The process is typically performed in an electrochemical cell setup, where aniline monomers undergo oxidation at the

working electrode, leading to polymer film formation.

Electrochemical Techniques for Polymerization

Electrochemical polymerization of aniline can be achieved through three primary techniques:

Galvanostatic Method:

- Polymerization occurs at a constant current applied between the working and counter electrodes.

- The reaction rate is controlled by the applied current, influencing the thickness and morphology of the resulting PANI film.

- This method is advantageous for producing uniform polymer coatings and well-defined film structures.

Potentiodynamic Method (Cyclic Voltammetry):

- In this technique, the electrode potential is varied cyclically over a range of voltages while the reference electrode measures the corresponding current.

- The oxidation and reduction behavior of aniline monomers is monitored, allowing insight into polymer growth dynamics.

-This method is commonly used for studying reaction mechanisms and optimizing polymerization conditions.

Potentiostatic Method:

- A constant potential is applied between the working electrode and the reference electrode, controlling the rate of monomer oxidation.

- This method allows precise control over the polymerization process, influencing conductivity, morphology, and doping levels.

- It is particularly useful for depositing uniform PANI films on electrode surfaces.

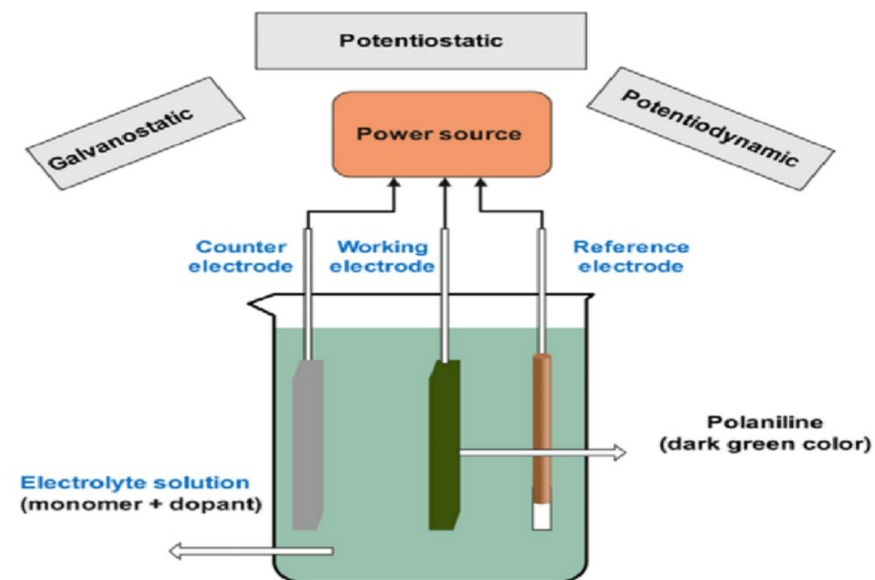Figure 2 illustrates a typical electrochemical cell setup used for the electro-polymerization of aniline.

FIGURE 2: Electrochemical cell setup for electro-polymerization of aniline

Mechanism of Electrochemical Polymerization

The electrochemical polymerization of aniline involves a multi-step oxidation process at the working electrode, resulting in the formation of a conjugated polymer network. The key stages in this mechanism are:

Monomer Oxidation:

- Aniline undergoes oxidation at the anode, generating a primary cation radical.

- This step is critical for initiating polymer growth and is influenced by the applied potential and electrolyte composition.

Dimer Formation:

- The cation radicals undergo deprotonation and re-aromatization, leading to the formation of aniline dimers.

- These dimers serve as building blocks for subsequent polymer growth.

Polymer Chain Growth:

- Further oxidation of dimers produces new cation radicals, which react with additional aniline monomers.

- This chain-growth process continues, leading to the development of extended conjugated structures.

Doping and Structural Formation:

- The final step involves spontaneous doping, where the polymer incorporates counterions from the electrolyte.

- The resulting doped PANI consists of alternating reduced (benzene ring) and oxidized (quinoid ring) units, which are responsible for its electrical conductivity.

Figure *3* illustrates the detailed mechanism of aniline electrochemical polymerization, highlighting the transformation from monomer oxidation to the formation of the conducting polymer network [8,9].
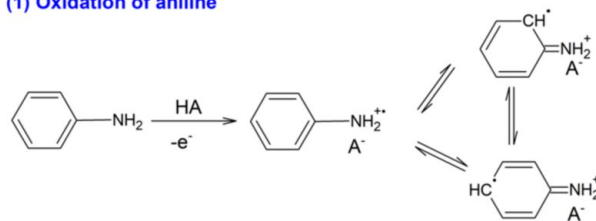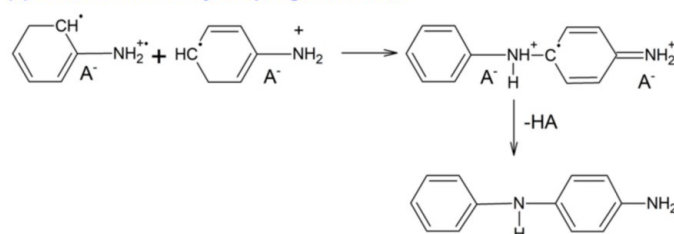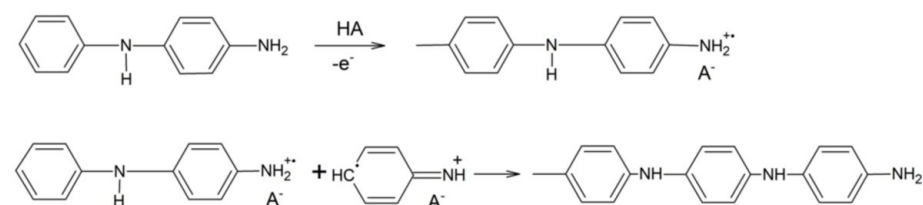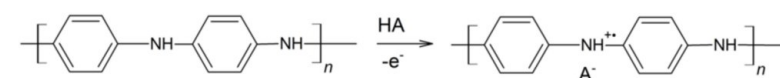
(1) Oxidation of aniline

(2) Dimer formation by coupling of radicals

(3) PANI propagation

(4) PANI doping

FIGURE 3: The mechanism of aniline electrochemical polymerization reaction

PANI, polyaniline

Key Advantages of Electrochemical Polymerization

- Precise Control: The applied potential or current determines polymer structure, conductivity, and thickness.

- Direct Deposition: Enables in-situ polymerization on conductive substrates, eliminating post-synthesis processing.

- Environmentally Friendly: Avoids the use of chemical oxidants and minimizes waste production.

- Enhanced Purity: The polymer obtained is free from residual oxidants and unwanted byproducts.

Potentiostatic Electrochemical Polymerization

Potentiostatic electrochemical polymerization is widely used for synthesizing PANI due to its precise control over the polymer's morphology, conductivity, and electrochemical properties. By applying a constant potential between the working electrode and the reference electrode, the polymerization process is regulated to achieve the desired film characteristics. Different electrode materials, electrolytes, and voltages applied using the potentiostatic method are shown in Table *1*. The effect of different conditions on the electro-polymerization of PANI is summarized in Table *2*.

Dopant acids and their effect on PANI electrodes: PANI was coated on a carbon cloth electrode using electrochemical polymerization, and the effect of various dopant acids on PANI's electrochemical

characteristics was investigated. The following dopant acids were studied:

- Hydrochloric acid (HCl)

- Perchloric acid ($HClO_4$)

- Sulfuric acid (H_2SO_4)

- p-Toluene sulfonic acid (p-TSA)

- Phosphoric acid (H_3PO_4)

- Phytic acid (PA)

Among these, PANI doped with $HClO_4$ exhibited the best capacitive behavior and energy storage capacity, with the longest discharge time. On the other hand, PANI doped with p-TSA demonstrated the best cycling stability, making it suitable for applications in supercapacitors and energy storage devices [11-13].

Nanocomposite formation and corrosion protection: The incorporation of reduced graphene oxide (rGO) into the PANI polymer enhanced the electro-polymerization process and improved the corrosion resistance of the PANI/rGO coating on aluminum alloy. The resulting PANI-rGO composite exhibited superior anticorrosion properties, making it an ideal protective coating for metal surfaces [14].

Effect of applied potential on PANI/graphene nanocomposites: The synthesis of PANI/graphene nanocomposites on PET-ITO (Polyethylene terephthalate -Indium tin oxide substrate) substrates was studied under various applied potentials ranging from 1.4 V to 2.2 V. The following observations were indicated:

- At potentials below 1.4 V: No deposition of PANI/graphene films occurred.

- At 2.0 V: Maximum conductivity (0.375 S/cm) was achieved with an increase in film thickness.

- At 2.2 V: The PANI structure began to degrade due to overoxidation, leading to polymer chain breakage [15].

Recycling electrolytes for sustainable PANI synthesis: The reuse of spent electrolyte solutions in electrochemical polymerization was explored as a cost-effective and environmentally friendly approach. While fresh electrolytes produced highly conductive PANI nanowires (576.6 F/g), spent electrolytes contained polymerization byproducts like p-hydroquinone and p-benzoquinone, which altered the polymer morphology, reducing its specific capacitance (457.5 F/g). The purity of electrolyte recovered using n-octanol and 2-octanone was used as extraction solvents, enabling the synthesis of high-purity PANI nanowires with capacitance close to fresh electrolyte conditions [16].

Comparison of chemical vs. electrochemical polymerization: A comparative study between chemical and electrochemical polymerization of PANI revealed that:

- Electrochemically synthesized PANI had more benzenoid rings, a higher molecular weight, and a lower bandgap energy.

- The solubility of PANI was influenced by the synthesis process, affecting oxidation efficiency and polymer chain configuration.

- The thermal stability of chemically and electrochemically synthesized PANI was nearly identical [17].

Solubility and protective coating properties: PANI synthesized under a 1.7 V potential with sulfuric acid doping exhibited different solubility behaviors in various solvents:

- Soluble in: NMP (N-methyl-2-pyrrolidone) and DMSO (dimethyl sulfoxide).

- Insoluble in: Acetone and chloroform.

Optimization of electrochemical deposition conditions: PANI films were deposited on a carbon cloth electrode at 0.9 V, with deposition times of 300 s, 600 s, 900 s, and 1200 s. The highest specific capacitance was observed at 600 s, making PANI/carbon cloth an excellent low-cost electrode material for supercapacitor applications and biosensors [18].

Effect of working electrodes and acids on PANI growth: The electrochemical synthesis of PANI thin films was studied using various working electrodes (Pt, Ti, Ni, SnO$_2$-coated glass) and different acids (HCl, HClO$_4$, p-TSA, H$_2$SO$_4$). Among them, PANI films formed in HClO$_4$ (1 M) showed the best growth rate and high-quality deposits [19].

Structural and electrical properties of PANI thin films:

- Glass/FTO (fluorine-doped tin oxide) substrates were used for electrochemical deposition.

- The electrical resistivity of PANI increased as pH changed from 2.0 to 6.5.

- The highest crystalline structure was observed at 1654 mV cathodic potential.

- Heat treatment at 300°C for 5 minutes enhanced crystallinity, but exceeding this temperature led to degradation [20].

Metal oxide nanoparticles in PANI electrodes: Metal oxide nanoparticles such as Zinc Oxide (ZnO), Iron (III), and Polyaniline Zinc Ferrite (ZnFe$_2$O$_4$) were used to modify PANI hybrid electrodes. The ZnFe$_2$O$_4$ nanoparticles improved porosity and charge storage capacity, making PANI/ZnFe$_2$O$_4$ composites excellent candidates for supercapacitor electrodes [21].

Electrode material	Applied potential (V)	Electrolyte	Film properties	Applications	Reference
Carbon cloth	0.9 V	HClO$_4$	High capacitive behavior	Supercapacitors	[10]
Al Alloy	1.4–2.2 V	rGO-PANI	Corrosion resistance	Protective coating	[11]
PET-ITO	2.0 V	Graphene-PANI	Max conductivity 0.375 S/cm	Flexible electronics	[12]
Glass/FTO	1.65 V	HCl, HClO$_4$	Highly crystalline PANI	Thin film solar cells	[17]
ZnFe$_2$O$_4$-PANI	Various	H$_2$SO$_4$	Improved charge storage	Supercapacitors	[18]

TABLE 1: Properties and applications of PANI films produced using the electrochemical potentiostatic method

PANI, polyaniline; PET-ITO, Polyethylene terephthalate substrate-Indium tin oxide; FTO, fluorine-doped tin oxide

Aniline conc.	Nano additives	Electrolyte		E. potential	Time (min)/Temp	WE	CE	RE	Washing and drying	Characterization devices	Application	Ref.
		Type	Conc.									
0.1 M	-	HCl, HCLO$_4$ H$_2$SO$_4$, PTSA, H$_3$PO$_4$, PA	0.5 M	1 V	5	Carbon cloth 1 cm × 2 cm	Pt mesh	Ag/AgCl	DI water 60°C	SEM/FTIR/XPS/electrochemical analyzer	Supercapacitor	[13]
0.4 M	r(GO) 0.03 gm	H$_2$SO$_4$	0.5 M 300 ml	1.4 V vs. SCE	30	Al alloy	-	-	-	Stereoscopic-microscope, SEM/TEM/FTIR, XPS	Corrosion	[14]
0.2 M	Graphene nanosheet 1 mg/ml	H$_2$SO$_4$	0.5 M	1.4, 1.6.1.8,2.2.2 V	8	PET-ITO 5 mm × 5 mm	Pt sheet	SCE	Dilute H$_2$SO$_4$ then DI water 60°C-24 h	Four-point probe, SEM, EIS, FTIR, XPS	Counter electrode using for flexible dye-sensitized solar cell (DSSC)	[15]
0.25 M	-	H$_2$SO$_4$	0.75 M	1.58 V WE = 0.90 V vs. SCE	20/20°C	SS 2.0 cm × 3.0 cm	SS 2.0 cm × 3.0 cm	SCE	DI water	SEM, UV vis, cyclic voltammetry	-	[16]
3.1 ml 0.15 M	-	DI Water HCl	199 ml 20 ml (1 M)	0.7 V vs. SCE	120	Graphite rod L= 15 cm D = 0.7 cm	SS L = 13 cm W = 2 cm t = 0.03 cm	SCE	Treated with ammonia and re-doped with PTSA	SEM, XRD, FTIR, TGA, UV	-	[17]

TABLE 2: Different conditions used in electrochemical polymerization of PANI using potentiostatic method

PANI, polyaniline; PET-ITO, polyethylene terephthalate substrate-Indium tin oxide; PTSA, p-toluene sulfonic acid; SCE, saturated calomel electrode; SEM, scanning electron microscope; XRD, X-ray diffraction; FTIR, Fourier transform infrared spectroscopy; TGA, thermal gravimetric analysis; UV vis, ultraviolet spectrophotometer; XPS, X-ray photoelectron spectroscopy; DI, distilled water; EIS, Electrochemical impedance spectroscopy; PA, Phytic acid

Galvanostatic Electrochemical Polymerization

The PANI electrode was successfully fabricated via galvanostatic polymerization of aniline on a cost-effective graphite electrode, using sulfuric acid as the dopant source. The polymerization was carried out at a current density of 2.0 mA/cm². During charge/discharge cyclic voltammetry experiments, the anodic potential limit was set to 0.5 V to achieve the emeraldine state while preventing further degradation. The PANI electrode exhibited 98% Coulombic efficiency and retained 95% of its original capacity, demonstrating high cyclic stability with minimal capacity loss [22]. Additionally, PANI films with different morphologies were synthesized using the galvanostatic method by altering the disc electrode's rotational speed. The mechanism of nano-PANI film creation was studied, including how the disk electrode's rotation speed affects the overall shape. This nano-PANI film was evaluated as an effective electroactive material for a model energy-storage device [23]. The electro-deposition of PANI and copper ions was successfully deposited on carbon paper to produce a low-cost cathode for low-temperature fuel cells (LTFCs). The incorporation of copper into the coating of PANI led to improvement of the oxygen reduction reaction (ORR) activity for fuel cells [24]. Table *3* presents the electrochemical polymerization parameters of PANI using the galvanostatic method.

Aniline Conc.	Electrolyte		Current Density (mA/cm^2)	Time/Temp	WE	CE	RE	Washing and drying	Characterization devices	Application	Ref.
	Type	Conc.									
0.25 mol/dm^3	H$_2$SO$_4$	1 mol/dm^3	2	22°C	Graphite cylinder A = 0.32 cm^2	Pt mesh	SCE	Bi distilled water	Cyclic voltammetry, EIS	Energy storage	[22]
0.2 M	HNO$_3$	1.0 M	2	500 s	SS Disk D = 6 mm	Graphite D = 1 cm	-	-	SEM, EIS	Energy storage	[23]
0.4 M	HNO$_3$ Copper (II) sulfate	0.7 M 0.6 M	2.5	-	Carbon paper A = 7.5 cm^2	Copper foil	Ag/AgCl	-	XPS, FTIR, SEM	Catalyst for fuel cells	[24]

TABLE 3: Electrochemical polymerization parameters of PANI using galvanostatic

PANI, polyaniline; SEM, scanning electron microscope; XPS, X-ray photoelectron spectroscopy; FTIR, Fourier transform infrared spectroscopy; EIS, Electrochemical impedance spectroscopy; SCE, saturated calomel electrode

Potentiodynamic (Cyclic Voltammetry)

PANI films were created by an electrochemical polymerization process using a glassy carbon electrode as the working electrode and a platinum electrode as the counter electrode. The PANI layer deposited on a glassy carbon substrate is polycrystalline, according to X-ray diffraction (XRD) investigations. Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR) measurement confirmed the formation of PANI film in a conducting state. The polymer morphology revealed a fibrous structure [25].

Using cyclic voltammetry (CV) in a potential range from -0.3 to 1 V, the electro-polymerization of PANI was carried out in an acidic medium (1 M HCl) containing 0.1 M aniline. The CV data indicate that the monomer is oxidized at a high positive potential (0.9 V against Ag), that the PANI film is continuously growing, and that the three most well-known forms of PANI redox are changing in the potential range between −0.3 V and 1 V. Additionally, the spectroscopic analysis verified the oxidation of PANI production. The final conductive PANI product, emeraldine salt, was created during the polymerization process as a result of the formed charge carriers, polarons and bipolarons, as indicated by the spectroscopic results [11].

The effects of using different concentrations of aniline monomer (0.05, 0.1 M, and 0.15 M) and different concentrations of doping acid HCl were studied. The findings indicate that low monomer concentrations (below 0.1 M) are optimal for high-quality polyaniline films with smooth surfaces, improved adhesion, reduced porosity, and uniform distribution, even though the rate of polymerization is low at these concentrations. Aniline at greater concentrations (0.15 M) polymerizes at a faster pace, but the film surface is flaky, uneven, and rough, and it adheres to the electrode poorly. The results of cyclic voltammetry demonstrate that the polymer films undergo oxidation in the potential range of 1-2 V and reduction (deprotonation) in the range of 0-2-0.8 V [26].

PANI films are doped with copper ions using various concentrations of copper sulfate. Experimental findings indicated that the film of polyaniline containing various transition metal ions differs in terms of its electrochemical characteristics, such as the form of its oxidation-reduction peaks and the current of its first anodic peak, but copper ions involved can enhance the electrochemical characteristics of PANI collectively. The existence of copper ions functioned as a redox-active catalyst. The p-p interaction between copper ions and PANI, which can boost PANI's delocalization and hence increase its electrical conductivity, is primarily responsible for the improvement of PANI characteristics. PANI doped with 0.2 M copper sulfate showed high specific capacitance when compared with PANI only, making it a good choice for supercapacitor applications [27].

PANI films were electrochemically deposited on a platinum (Pt) electrode in an H$_2$SO$_4$ solution containing aniline monomer. The rate of polymerization increases with increasing monomer content. For films made in more diluted monomer solutions, the aniline concentration of 0.1 M has three identified initial redox waves with noticeably larger current densities for redox reactions between these various species [28]. Electrodeposition of titanium oxide (TiO$_2$) nanoparticles and PANI on a platinum electrode was performed using an electrolyte of 1 M H$_2$SO$_4$. The potential of CV was in the range of -0.4 to 1 V, but the electrodeposition from the results occurred at 0.7 V/SCE for PANI without and with TiO$_2$ nanoparticles. The existence of TiO$_2$ in PANI composite films has a higher irreversibility because the TiO$_2$ nanoparticles reduce the composite film's electrical conductivity. Also, due to the presence of TiO$_2$, the oxidation process linked to polymers is inhibited, and the degradation products in composite materials are reduced.

Composite materials adhered well to the Pt electrode and had better electro-active repetitive qualities than pure polyaniline [29].

The impact of selecting a working electrode type on the electrochemical polymerization process was examined using two distinct working electrodes: a platinum plate and a silver electrode. Platinum wire was used because PANI film does not develop on the silver electrode in the potential range between -100 mV and 900 mV. Additionally, CV results and the study of monomer concentration variation showed that high monomer concentrations lead to faster polymerization rates, flaky, rough surfaces, and poor adhesion. Therefore, the monomer concentration (0.1 M) should be maintained [30].

For the creation of PANI and carbon nanotube CNTs composites, several CNT concentrations were employed. The produced composite films have a porous network structure that can help with ion transmission and provide additional avenues for electron transport. The conductivity rose as the concentration of CNTs increased until 5.5 weight percent. But due to its coloring efficiency and electrochromic property, optimal results were observed at 3.5 weight percent CNTs. The development of electrochromic materials was made possible by using PANI/CNT composite films [31].

It is feasible to deposit PANI on the interior surface of 3D organized macroporous carbon (working electrode) acting as a host matrix. The incorporation of organic functional groups may result in interesting applications in photoelectron devices, and the host carbon can act as a support [32].

PANI and polyacrylic acid (PAA) hybrid films were prepared under the potential of CV between -0.4 and 0.9 V. The conductivity measurements showed that the carboxyl groups in PANI/PAA films lowered the conductivity of the polymeric films, but the films also helped to protonate the nitrogen atoms of PANI, increasing the electroactivity of the films in neutral solution. PANI films modified with carboxyl groups of PAA made it suitable for bio-electrochemical devices, such as biosensors and biofuel cells [33].

Electrochemical behavior, electro-catalytic activity, and stability of the PANI deposition on bare Al and pre-treated electrode with hexa-chloroplatinic acid (H_2PtCl_6) solution (Al-Pt electrode) were studied. No deposition of PANI occurred on the bare Al electrode using low aniline concentrations (0.02-0.35 M), and deposition occurred at concentrations above 0.35 M. While using the Al-Pt electrode, the PANI film starts to form at low concentrations of aniline, and the growth rate increases with monomer concentration. The thickness of the polymer on the Al-Pt is larger than that of bare Al or even a smooth Al-Pt electrode for all monomer concentrations. It is advised to use a reasonable concentration of H_2SO_4 (0.1 M) as electrolyte for the electrosynthesis of PANI on the Al electrodes to avoid the development of reaction intermediate products. PANI growth rate for various pretreatment times ranging from 10 to 180 s shows that the growth rate is almost independent of the Al electrode pretreatment time, so a short duration of 10 s is preferred [34]. Table *4* shows that different studies have investigated the electrochemical polymerization conditions of PANI using the potentiodynamic method.

Aniline Conc.	Nano additives	Electrolyte		Cyclic voltammetry	Time (min)/Temp	WE	CE	RE	Washing and drying	Characterization devices	Application	Ref.
		Type	Conc.									
0.1 M	-	H_2SO_4	0.5 M	-0.2 V and 1.2 V (Ag/AgCl) cycles no. = 15	Room temp.	Glassy carbon	Pt	Ag/AgCl	DI water	Cyclic voltammetry, SEM, XRD, Raman spectroscopy, FTIR	-	[25]
0.1 M	-	HCl	1 M	-0.3 to 1 V Scan rate = 50 mV s^{-1}		(Au-SPE) Metal	Pt	Silver	-	-	-	[11]
0.05 M, 0.1 M, 0.15 M	-	HCl	0.5 M 1 M (opt.) 1.5 M 2.0 M	-100 mV to 1400 mV Scan rate = 25 mV/s Cycles no. = 40	-	SS	SS	SCE	-	Cyclic voltammetry, FTIR	-	[26]
0.2 M	-	H_2SO_4 $CuSO_4.5H_2O$	0.5 M 0.1, 0.2, 0.3, 0.4 M	-0.2 V to 0.9 V cycles no. = 71	Room temp.	SS mesh 1 cm x 1 cm	Pt	SCE	0.5 M H_2SO_4/60°C 12 h	SEM, XRD, FTIR, XPS, EDS, Cyclic voltammetry, EIS	Supercapacitor	[27]
0.1 M	-	H_2SO_4	1 M	-0.24 and 0.9 V/SCE Scan rate = 50 mV/s	Room 20°C	Pt wire 0.2 cm^2	Carbon glassy	SCE	Double DI water	Cyclic voltammetry	-	[28]
0.1 M	TiO_2 21 nm 0.01 M	H_2SO_4	2 M	-0.4 to 1 V (SCE) (Polymerization occurred at 0.7 V)		Pt disc sealed in glass 24 mm^2	Pt coil	SCE	-	-	-	[29]
0.1 M	-	HCl $HClO_4$ PTSA H_2SO_4	1 M 1 M 1 M 0.5 M	-0.2 to 1.0 V vs Ag/AgCl Cycles No. = 100–150 Scan rate = 100 mV/s		Pt, Ni, Ti, and SnO_2 coated Glass plates	Pt mesh (2 cm x 2 cm)	Ag/AgCl	-	Cyclic voltammetry	-	[19]
Anilinum hydrochloride 0.4 M	-	HCl	-	-100 mV to + 900 mV vs. SCE	25°C	Pt plate 1 cm × 1 cm Silver plate	Pt wire	KCl SCE	-	Cyclic voltammetry	-	[30]
0.1 M	-	H_2SO_4	1 M									
0.25 M	CNTs (0.5-5.5 wt.%)	Ethyl alcohol Dodecyl benzene sulfonic acid (DBSA)	5 mol/L 0.6 mol/L	-0.2 to 1.0 V scan rate = 56 mV/s		ITO film/PET substrate	Pt sheet	SCE	-	SEM, FTIR, cyclic voltammetry, four probe, UV	Electrochromic materials	[31]
0.1 M	-	H_2SO_4	2 M	-	-	Macroporous carbon	Pt wire	Ag/AgCl	Deionized water 50°C	-	Photoelectron devices	[32]
0.5 M	-	H_2SO_4 Poly acrylic acid (PAA)	0.5 M 0, 2.9, 9.4, 13.5, 18.2 wt.%	-0.4 to 0.9 V vs. SCE scan rate = 0.05 V/s		A gold film deposited on a quartz plate A = 0.25 cm^2	Pt plate	SCE	0.5 M H_2SO_4 distilled water	SEM/four probe/cyclic voltammetry	Bio-electrochemical devices (biosensors and biofuel cells)	[33]
20–500 mM	-	H_2SO_4	0.1 M	-0.2 to 1.0 V Scan rate = 50 mV s^{-1} cycles No. = 10 or 24		Al or Al–Pt D = 3 mm	Pt wire	SCE	-	SEM/cyclic voltammetry	-	[34]

TABLE 4: Electrochemical polymerization of PANI conditions using potentiodynamic method

SEM, scanning electron microscope; XRD, X-ray diffraction; FTIR, Fourier transform infrared spectroscopy; SCE, saturated calomel electrode; DI, distilled water; PANI, polyaniline; EDS, energy dispersive spectroscopy

PANI nanocomposite and applications

When two or more materials with considerably differing properties are mixed, a new substance known as a composite is created. The new materials (composites) that are produced have attributes that are either superior to or distinct from the original materials. This is done to bring out a new material with improved characteristics [35,36]. PANI has exceptional characteristics and attraction, but in certain applications, it

has certain drawbacks. Enhancing PANI, for example, by mixing it with other materials to create polymeric composites, is crucial to achieving greater efficiency across a range of applications. Polymeric composites are the final product of mixing materials with polymers; hence, a new substance that has been added and has nanoscale dimensions is referred to as a polymeric nanocomposite [37,38].

Nanoparticle materials could be carbon nanomaterials, including single-walled carbon nanotubes (SWCNT), multi-walled carbon nanotubes (MWCNT), carbon nanofibers, carbon nano-spheres, graphene, and graphene oxide [39-42]. Also, they could be metal or metal oxide nanoparticles, such as gold, platinum, palladium, and silver, with different compositions and dimensions [29,43-47]. Many attempts have been made to enhance the mechanical and electrical properties of polymers by combining conducting polymers with nanoparticles. The incorporation has been explored to produce functional nanocomposite materials with superior properties for fundamental and technological perspectives [48-50]. The nanoparticle materials could be carbon materials, metal, or metal oxides. Carbon nanomaterials, such as graphene and graphene oxide, carbon nanofibers, carbon nanospheres, SWCNT and MWCNT, and graphene [11,43-44]. Metal or metal oxide nanoparticles, such as gold, platinum, zinc, palladium, and silver, are commonly used [21,37,51].

The synthesized PANI nanocomposites have been put to productive use in a variety of applications and have shown excellent performance in applications such as sensors, supercapacitors, photonic devices, electrode materials, and catalytic applications. Furthermore, there is a vast array of PANI polymeric nanocomposites with various applications and polymerization processes, as well as a variety of shapes and structures. This is obvious evidence of the significance of PANI and its numerous applications in both the experimental and industrial sectors. PANI nanocomposite materials using different nanoparticles, different conditions of preparation, and applications are summarized in Table 5 using the electrochemical polymerization method.

Composite	Electrolyte	Electrodes	Time	Temp.	Washing	Drying	Characterization	Application	Ref
PANI-WCNTs	AN 0.3 M H_2SO_4 0.1 M f-SWCNTs 0.005 and 0.01% Distilled water 150 ml	WE: titanium plate RE: indium tin oxide (ITO) Voltage = 2.4 and 2.2 V	3 min				Interferometer technique, XRD, SEM, FTIR	H_2S sensing	[52]
PANI-rGO	AN 0.4 M H_2SO_4 0.5 M rGO 0.03 g	WE: 5083 Al alloy Potentiostatic 1.4 V vs. SCE	1800 s		Scraped off the Al surface		SEM, TEM, FTIR, XPS, EIS	Corrosion protection	[14]
PANI-Au	AN 0.003 M AuNPs 25 mg/l	WE: Pt Cyclic voltammetry: scan rate: 0.05 V/s sweeping potential: 0.5 to 1.0 V		Room			TEM, SEM, UV-vis spectroscopy, FTIR, dynamic light scattering (DLS, cyclic voltammetry, EIS)	Electrochemical aptasensor: or the sensitive determination of lysozyme in human serum and urine	[51]
PANI-MnO_2	H_2SO_4 Manganese sulfate ($MnSO_4$) Distilled water acetone	Potentiostatic Voltage: 1.1 V/Ag/AgCl	500 s	Room			FTIR, SEM, contact angle, EIS	Electrochemical Supercapacitor	[53]
PANI-CuO	AN 0.2 M (1.0 ml) HCl 1 M (40 ml) APS 0.2 M (2 g) CuO 0.05, 0.2, 2 g	WE: carbon CE: platinum RE: silver Voltage: 2 V	15 min		Distilled water	60°C/24 h		Supercapacitor and energy storage device applications	[54]
PANI-CuO		Voltage: 2V	15 min				FTIR, SEM, TEM		[55]
PANI-CoO (cobalt oxide)	CoO 0.4wt%	Voltage: 2V	16 min				SEM, UV, Cyclic voltammetry		[56]
PANI-NiO (nickel oxide)	AN 0.005 $NiSO_4$ 0.2 M	Cyclic voltammetry -0.3 to1.2 V vs. SCE at 50 mV/s					SEM, EDX, EIS		[57]
PANI-carbon fiber	AN 0.1, 0.25, 0.35, 0.5 M PTSA 0.1, 0.25, 0.5, 0.65, and 0.8 M	WE: 6KT650/35 carbon fibers CE: SS plate RE: SCE Cyclic voltammetry: -0.2 V to 0.1 V SCE, scan rate: 20, 30, 50, 100 mV/s	10-50 min		Deionized water	Room temp. 24 h 100 C/1 h	FTIR		[58]

PANI-V_2O_5	AN 0.1 M H_2SO_4 2 M vanadyl sulfate 0.05, 0.1, 0.2, 0.3, 0.4, and 0.5 M	WE: carbon cloth (1 cm^2) CE: carbon cloth RE: SCE -0.2 and 0.9 V scan rate 20 mV s^{-1}		Distilled water	50 C for 24 h	SEM, XRD, FTIR, EDX, EIS	Supercapacitors	[59]
PANI-Fe_2O_3-ZnO PANI-ZnO PANI-Fe_2O_3	AN 1.0 mL, 10.9 mmol H_2SO_4 5.55 mL, 1 M DBSA 0.5 mL, 2.2 mmol ZnO and Fe_2O_3 1:2 ratio (1 gm) Total volume with water = 100 ml	WE: gold RE: SCE 0.8 V vs. SCE	600 s	Distilled water acetone		SEM, EDX, UV vis, FTIR, EIS	Electrode materials for supercapacitors	[21]
PANI-Au-nafion	AN 0.1 M HCl 1 M or H_2SO_4 0.5 M AN 0.1 M $HClO_4$ 1 M	CE: Pt wire RE: Ag/AgCl cyclic voltametry: scanning rate and 20 mV s^{-1} range: −200 to 1200 mV Constant current density 1,5, 10 mA/cm^2	30				NO_2 gas sensor	[60]
PANI-SWCNT	AN 0.325 M H_2SO_4 1 M SWCNT 5 ml (0, 2, 4, 8 wt%)	WE: A platinum plate (0.8 cm) CE: Pt wire (0.07 cm) RE: (SCE) Cyclic voltammetry: -0.20 to 1.20 V scan rate 100 mv/s		Room temp.		SEM, AFM, UV, EIS, FTIR		[61]

TABLE 5: PANI nanocomposites materials synthesis using different nanoparticles using electrochemical polymerization

SCE, saturated calomel electrode; SEM, scanning electron microscope; XRD, X-ray diffraction; FTIR, Fourier transform infrared spectroscopy; EIS, Electrochemical impedance spectroscopy; XPS, X-ray photoelectron spectroscopy; TEM, Transmission Electron Microscopy; PTSA, p-toluene sulfonic acid; UV vis, ultraviolet spectrophotometer

Electrochemical polymerization modeling

A mathematical model between conductivity and reaction parameters (monomer concentration, acid concentration, applied potential, reaction time, and reaction temperature) was used via regression analysis. With the use of the Origin program, both linear and polynomial single regression as well as multiple linear regression analyses were performed, and the relations were obtained. The output (DC conductivities) derived from the correlation models agrees well with the findings of the experiments. All of the generated R^2 (correlation coefficient) or Ra^2 values (coefficient of multiple determination) are closer to 1. The models for the relations between conductivity and other parameters are shown below [62]:

Model equation between conductivity σ and acid concentration (A):

$$\sigma = a + b_1 A + b_2 A^2 + b_3 A^3 + b_4 A^4 \ (1)$$

$$\sigma = -0.000908333 + 0.01905A - 0.06981A^2 + 0.11809A^3 - 0.06626A^4, \quad R^2 = 0.9965 \ (2)$$

Model equation between conductivity σ and acid concentration (H):

$$\sigma = a + b_1 H + b_2 H^2 + b_3 H^3 + b_4 H^4 + b_5 H^5 + b_6 H^6 (3)$$

$$\sigma = -0.00276 + 0.02259H + 0.06075H^2 + 0.0748H^3 - 0.0440H^4 + 0.0122H^5 - 0.00129H^6, \quad R^2 = 0.9818(4)$$

Model equation between conductivity σ and reaction temperature (T):

$$\sigma = a + bT(5)$$

$$\sigma = 0.00193 - 0.0000309399T, \quad R = -0.9745(6)$$

Model equation between conductivity σ and reaction time (t):

$$\sigma = a + b_1 t + b_2 t^2 + b_3 t^3(7)$$

$$\sigma = -0.00196 + 0.00176t - 0.000187635t^2 + 0.00000574998t^3, \quad R^2 = 0.9948 (8)$$

Model equation between conductivity σ and potential applied (V):

$$\sigma = a + b_1V + b_2V^2 (9)$$

$$\sigma = -0.00504 + 0.01061V - 0.00475V^2, \quad R^2 = 0.9597 (10)$$

Where: a and b are constants; σ is DC conductivity; A, monomer concentration (M); H, HCl concentration (M); T, temperature (8C); t, time (h); V, applied potential (V); R, correlation coefficient; R2, coefficient of multiple determination.

A mathematical model was used to study the electrochemical characteristics of PANI thin film formed on the electrode surface and the electrolyte. The study investigated the redox reaction and doping/redoping process to produce PANI forms from leucoemeraldine to emeraldine salt using cyclic voltammetry. The model suggested that the interaction between PANI thin film and electrolyte is passing through three steps: the transformation of LB to EB due to reduced sites being converted to oxidized sites, the diffusion of anions (A⁻) from the electrolyte toward the PANI film, and the adsorption process where EB is transformed to ES by the adsorption of the dopant anions (A⁻) on the oxidized sites of film. The model combined the Fickian second law, conventional diffusion, Langmuirian adsorption, and nemest equation to obtain the following equation [63]:

$$\frac{d\Gamma_{OA}}{dt} = K_{ad}C_A \left[\frac{\Gamma^* - \Gamma_{OA}}{1 + C_H \exp\left(\frac{-nF(E-E^{0'})}{RT}\right)} \right] - K_{de}\Gamma_{OA} (11)$$

Where ΓOA is the surface concentration of doped sites (adsorbed site by dopant), t for time, K_{ad} is the adsorption rate constant, CA is the bulk concentration of dopant, CH is the concentration of hydrogen ions, E (in V) is the electrode potential, E0' (in V) is the formal potential of the PANI redox reaction, R_g (in J mol^{-1} K^{-1}) is the gas universal constant, T (in K) is the absolute temperature, and F is the Faraday constant.

Another mathematical model was created to investigate the electrochemical reactions taking place at electrodes coated with conducting polymer thin layers. The model used Fick's law to describe the diffusion of reactant into a polymer layer and chemical kinetics equations to describe the rate of reaction. The combination of equations results in the equations for the rate
equations for concentration of reactant (R), concentration of product (P), and the charge carrier [64]:

$$\frac{\partial R}{\partial t} = D\frac{\partial^2 R}{\partial x^2} - KR^n (12)$$

$$\frac{\partial P}{\partial t} = D\frac{\partial^2 P}{\partial x^2} + KR^n (13)$$

$$\frac{\partial n}{\partial t} = D_n\frac{\partial^2 n}{\partial x^2} - KRn, \quad x \in [0,d], \quad t > 0 (14)$$

Where x is a space coordinate, D is the diffusion coefficient for reactant, and F is faraday constant. Another equation obtained for the density I(t) of the current at time (t) is:

$$I(t) = n_eFD_n\frac{\partial n(0,t)}{\partial x} (15)$$

Conclusions

The electrochemical polymerization of PANI was successfully demonstrated using three distinct methods: galvanostatic, potentiostatic, and potentiodynamic (cyclic voltammetry). Each method has its advantages, limitations, and specific applications, as discussed in various studies.

1. Potentiostatic Polymerization:

- The choice of doping acid significantly impacts the electrochemical properties of PANI. PANI doped with perchloric acid (HClO$_4$) exhibited the highest capacitive behavior and longest discharge time, while p-

toluene sulfonic acid (p-TSA) improved cycling stability.

- The optimal potential range for PANI/graphene nanocomposites deposition on PET-ITO substrates was found to be 1.4-2.2 V, with maximum conductivity (0.375 S/cm) observed at 2 V. However, exceeding 2.2 V led to degradation and breakage of the PANI chain.

- Reuse of the electrolyte solution was investigated, showing that while PANI synthesized in fresh electrolyte had a high specific capacitance (576.6 F/g), PANI synthesized in recycled electrolyte after byproduct extraction retained 571.0 F/g, demonstrating a sustainable synthesis approach.

- The study of PANI deposition on carbon cloth electrodes revealed that the highest specific capacitance was achieved at 600 s under 0.9 V. This PANI/carbon cloth electrode exhibited good ascorbic acid detection and promising supercapacitor performance.

- Chemical or electrochemical re-doping with iodine or bromine gas increased the conductivity of PANI thin films from 10^{-9} Ω^{-1} cm^{-1} to 10 Ω^{-1} cm^{-1}, significantly enhancing its electrical performance.

2. Potentiodynamic (Cyclic Voltammetry) Polymerization:

- PANI was electrochemically synthesized in 1 M HCl with 0.1 M aniline, showing continuous film growth with oxidation potentials around 0.9 V (Ag/AgCl) and redox transitions in the range −0.3 V to 1 V.

- The concentration of aniline monomer and doping acid influenced the film quality:

0.05-0.1 M aniline yielded smooth, well-adhered films.

0.15 M aniline led to faster polymerization but resulted in rough, flaky films with poor adhesion.

- PANI films doped with 0.2 M $CuSO_4$ exhibited improved electrochemical properties due to enhanced charge delocalization, making them suitable for supercapacitors.

- The presence of TiO_2 nanoparticles in PANI composites improved the mechanical stability of the films but reduced electrical conductivity due to increased irreversibility.

- The incorporation of CNTs (3.5 wt%) into PANI films resulted in optimal electrochromic properties, enhancing their application potential in display technologies.

Electrochemical synthesis of PANI on Al-Pt electrodes demonstrated that the pre-treatment of aluminum enhanced adhesion and film thickness, with optimal results achieved at 0.1 M H_2SO_4 and a short pre-treatment time of 10 s.

Key Takeaways:

- Dopant selection plays a critical role in determining the capacitive behavior, cycling stability, and electrochemical performance of PANI.

- Optimized potential and monomer concentration lead to high-quality films with enhanced conductivity, adhesion, and electrochemical properties.

- Hybrid composites (PANI with graphene, CNTs, TiO_2, $ZnFe_2O_4$, and Cu^{2+} ions) significantly improve performance for applications in supercapacitors, corrosion prevention, and bio-electrochemical devices.

- Recycling electrolyte solutions for PANI synthesis is a sustainable approach without compromising electrochemical performance.

This study provides valuable insights into tailoring the synthesis conditions of PANI for specific applications, including energy storage, corrosion protection, biosensors, and electrochromic materials.

Additional Information

Author Contributions

All authors have reviewed the final version to be published and agreed to be accountable for all aspects of the work.

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Disclosures

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