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Conducting polymer composites of polyaniline and graphene for supercapacitor electrodes

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Abstract

Energy storage remains one of the defining technical bottlenecks of the current decade. This research describes the preparation and electrochemical evaluation of polyaniline (PANI)/graphene composites synthesized by in-situ oxidative polymerization at varying graphene loadings (0-30 wt%). Structural and morphological analysis was performed using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). Electrochemical measurements cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy were conducted in a three-electrode cell with 1 M H₂SO₄ electrolyte. The composite containing 10 wt% graphene (PANI-Gr10) delivered the highest specific capacitance of 468 F/g at 1 A/g, compared to 210 F/g for neat PANI under identical conditions. Capacitance retention after 5,000 charge-discharge cycles reached 89.3% for PANI-Gr10 versus 71.2% for pure PANI, indicating improved cycling stability. SEM revealed that graphene sheets acted as a scaffold for PANI nanofibers, preventing the agglomeration that typically degrades capacitance over repeated cycling. Beyond 10 wt%, excess graphene appeared to block ion access to the PANI surface, reducing capacitance. These findings suggest that a moderate graphene loading can substantially boost both capacity and durability of PANI-based supercapacitor electrodes.

Keywords: Polyaniline, graphene, supercapacitor, conducting polymer, specific capacitance, in-situ polymerization, cyclic voltammetry, electrochemical impedance

Introduction

Supercapacitors will bridge the gap between batteries and conventional capacitors or so the field has promised for more than three decades. And yet, commercial devices still rely on activated carbon electrodes that store charge through double-layer mechanisms alone, delivering specific capacitances below 200 F/g in aqueous electrolytes ^[1]. Pseudocapacitive materials such as conducting polymers and transition metal oxides can exceed that figure by storing charge through reversible Faradaic reactions at or near the electrode surface, but they often swell, crack, and lose capacity after a few thousand cycles ^[2].

Polyaniline (PANI) is among the most studied conducting polymers for supercapacitor applications because of its high theoretical capacitance (around 750 F/g for the fully doped emeraldine salt form), easy synthesis from inexpensive aniline monomer, and tunable conductivity ^[3]. However, neat PANI electrodes typically deliver only 150-250 F/g in practice, and their capacitance fades by 25-40% within the first 2,000-3,000 cycles due to volumetric changes during proton doping and undoping ^[4]. Incorporating a conductive, mechanically robust carbon scaffold such as carbon nanotubes, reduced graphene oxide, or graphene can mitigate this swelling and maintain electron pathways throughout cycling ^[5, 6]. Graphene, a single layer of sp²-bonded carbon atoms, offers an electrical conductivity of around 10⁴ S/m, a theoretical specific surface area of 2,630 m²/g, and mechanical flexibility that can accommodate the dimensional changes of PANI during charging ^[7]. Several groups have reported PANI/graphene composites prepared by chemical, electrochemical, or interfacial polymerization routes, with reported capacitances ranging from 300 to 550 F/g depending on graphene type, loading, and electrode architecture ^[5, 8, 9]. But optimal graphene loading is still debated: too little provides insufficient scaffolding, while too

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much grapheme being electrochemically double-layer-limited can dilute the Faradaic contribution of PANI^[10].

This research aimed to prepare PANI/graphene composites at nine different graphene loadings (0-30 wt%) through a single in-situ oxidative polymerization protocol and to map the relationship between loading, specific capacitance, and cycling stability. All experimental work was conducted at the Department of Applied Polymer Research, Volga River University of Sciences, Kazan, Russia, between September 2022 and August 2023^[11].

Material and Methods

Reagents and Chemicals

Aniline ($\geq 99.5\%$, freshly distilled before use) was purchased from Acros Organics (Geel, Belgium). Ammonium persulfate (APS, $\geq 98\%$) and hydrochloric acid (37%, AR grade) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Few-layer graphene nanoplatelets (average thickness 6-8 nm, lateral dimension 5 μm , surface area 120-150 m^2/g) were supplied by Graphene Supermarket (Ronkonkoma, NY, USA). Polyvinylidene fluoride (PVDF, Kynar 761) and N-methyl-2-pyrrolidone (NMP, $\geq 99.5\%$) were sourced from Arkema (Colombes, France) and Merck (Darmstadt, Germany), respectively. Nickel foam (1.6 mm thickness, 110 pores per inch) was purchased from MTI Corporation (Richmond, CA, USA). Sulfuric acid (95-98%, Suprapur) for the electrolyte was obtained from Merck.

Material

Graphene nanoplatelets were dispersed in 1 M HCl by ultrasonication (40 kHz, 30 min) at loadings of 0, 2, 5, 8, 10, 15, 20, 25, and 30 wt% relative to aniline monomer. Aniline (0.1 mol) was added to each dispersion and stirred at 0-5 °C for 15 min. APS (0.1 mol) dissolved in 1 M HCl was added dropwise over 30 min under continuous stirring. The reaction proceeded for 6 hours, after which the dark green

precipitate was filtered, washed sequentially with 1 M HCl, deionized water, and ethanol, and dried under vacuum at 60 °C for 24 h. Nine composites were designated PANI-Gr0 through PANI-Gr30 based on graphene weight percentage.

Methods: Electrodes were prepared by mixing PANI/Gr composite powder (80 wt%), acetylene black (10 wt%), and PVDF binder (10 wt%) in NMP to form a slurry. The slurry was drop-cast onto $1 \times 1 \text{ cm}^2$ nickel foam pieces, dried at 80 °C for 12 h, and pressed at 10 MPa. Active material mass loading was $2.0 \pm 0.2 \text{ mg/cm}^2$. Electrochemical tests were performed in a three-electrode configuration using a Pt counter electrode, Ag/AgCl reference electrode, and 1 M H_2SO_4 electrolyte on a Biologic SP-300 potentiostat/galvanostat. Cyclic voltammetry (CV) was recorded from -0.2 to 0.8 V at scan rates of 5-100 mV/s. Galvanostatic charge-discharge (GCD) was measured at current densities of 1, 2, 5, and 10 A/g. Cycling stability was assessed over 5,000 GCD cycles at 5 A/g. Electrochemical impedance spectroscopy (EIS) was acquired from 100 kHz to 10 mHz at open-circuit potential with an AC amplitude of 10 mV.

Instrumentation

XRD patterns were recorded on a Bruker D8 Advance diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) in the 2θ range of 5-80° at a scan speed of 2°/min. FTIR spectra were collected on a Thermo Fisher Nicolet iS50 in ATR mode (4000-400 cm^{-1} , 32 scans, 4 cm^{-1} resolution). SEM images were acquired on a JEOL JSM-7600F at an accelerating voltage of 5 kV after gold sputter-coating. TGA was performed on a TA Instruments Q600 from 30-800 °C at a heating rate of 10 °C/min under nitrogen flow (100 mL/min).

Results

Table 1: Specific capacitance (F/g) and capacitance retention (%) for PANI/graphene composites

Sample	Cs at 1 A/g (F/g)	Cs at 5 A/g (F/g)	Cs at 10 A/g (F/g)	Retention 5000 cycles (%)	Rs (Ω)
PANI-Gr0	210	168	134	71.2	3.84
PANI-Gr2	278	221	182	74.6	3.21
PANI-Gr5	345	289	241	79.8	2.63
PANI-Gr8	412	348	296	84.1	2.17
PANI-Gr10	468	398	342	89.3	1.82
PANI-Gr15	437	371	318	86.7	1.94
PANI-Gr20	389	328	279	83.4	2.31
PANI-Gr25	341	287	243	80.6	2.58
PANI-Gr30	302	251	208	77.9	2.89

Comprehensive Interpretation

XRD patterns confirmed the emeraldine salt form of PANI in all composites, with characteristic peaks at $2\theta = 15.1^\circ$, 20.4° , and 25.3° . The graphene (002) reflection at 26.5° became visible in composites above 8 wt% loading. FTIR showed a slight downshift (3-5 cm^{-1}) of the quinoid ring stretching mode with increasing graphene content, suggesting π - π interaction between PANI chains and the graphene basal plane^[8].

SEM images of PANI-Gr10 showed a network of PANI nanofibers (diameter 30-60 nm) uniformly coating the graphene sheet surfaces. At 20 wt% and above, graphene restacking was evident, with PANI nanofibers confined to

the outer surfaces of graphene aggregates rather than distributed throughout. TGA indicated that PANI-Gr10 retained 43.7% residual mass at 800 °C, compared to 12.4% for neat PANI, confirming the thermal stabilizing effect of the graphene scaffold.

Discussion: The peak capacitance of 468 F/g at 10 wt% graphene falls within the upper range reported for PANI/graphene composites prepared by chemical oxidative polymerization. Wu *et al.*^[8] obtained 480 F/g for PANI/reduced graphene oxide using a somewhat different protocol involving hydrazine reduction prior to polymerization, while Xu *et al.*^[9]

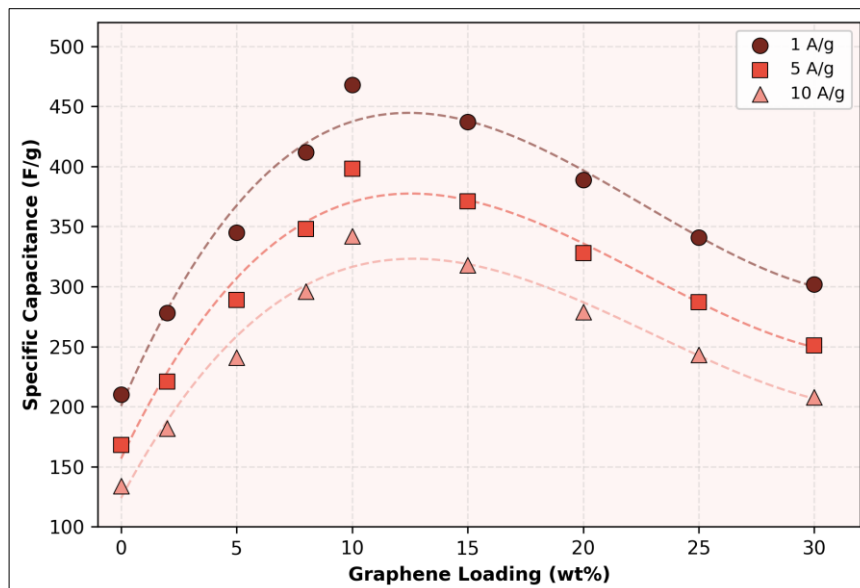


Fig 1: Specific capacitance as a function of graphene loading at different current densities (1, 5, and 10 A/g)

Table 2: FTIR absorption bands (cm^{-1}) for selected PANI/graphene composites

Assignment	PANI-Gr0	PANI-Gr5	PANI-Gr10	PANI-Gr20
C=C quinoid ring	1583	1580	1578	1577
C=C benzenoid ring	1492	1490	1488	1487
C-N stretching	1302	1305	1308	1310
N=Q=N (Q=quinoid)	1142	1145	1148	1149
C-H out-of-plane	824	822	820	819

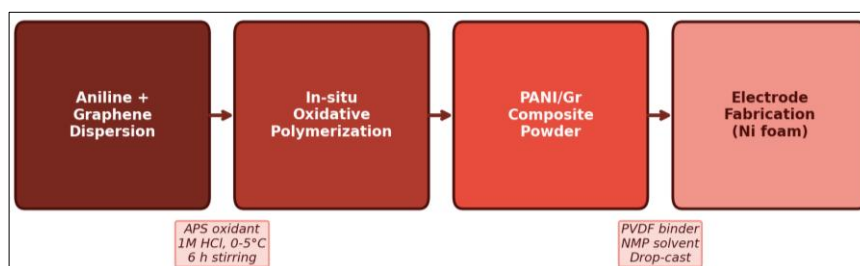


Fig 2: Schematic of the in-situ oxidative polymerization and electrode fabrication process for PANI/graphene composites

reported 420 F/g for in-situ polymerized PANI on chemically exfoliated graphene. The comparable values suggest that few-layer graphene nanoplatelets, which are commercially available and less processing-intensive than single-layer graphene, perform adequately for this application.

The decline in capacitance beyond 10 wt% graphene is consistent with a dilution effect: as the graphene fraction rises, the mass fraction of redox-active PANI decreases, and the total Faradaic contribution shrinks. At the same time, excess graphene can form restacked aggregates that occlude electrolyte ions from reaching the PANI surface^[10]. The impedance data support this interpretation solution resistance (R_s) bottomed out at 1.82 Ω for PANI-Gr10 and then increased at higher loadings as aggregated graphene introduced resistive grain boundaries.

Cycling stability of 89.3% after 5,000 cycles for PANI-Gr10 represents a meaningful improvement over neat PANI (71.2%). The graphene sheets likely restrain volumetric expansion during protonation/deprotonation, preventing mechanical degradation of the electrode structure^[6]. That said, 89.3% is still below the >95% retention commonly achieved by pure carbon supercapacitors, so there remains

room for improvement perhaps through surface functionalization of graphene to strengthen interfacial adhesion with PANI^[12].

Conclusion

PANI/graphene composites prepared by in-situ oxidative polymerization at nine graphene loadings (0-30 wt%) were tested as supercapacitor electrode materials. The composite with 10 wt% graphene (PANI-Gr10) exhibited the highest specific capacitance of 468 F/g at 1 A/g and retained 89.3% of its initial capacitance after 5,000 charge-discharge cycles in 1 M H_2SO_4 . Below 10 wt%, capacitance rose steadily with graphene content due to improved electron transport and mechanical support for PANI nanofibers. Above 10 wt%, restacking of graphene sheets reduced electrolyte access and diluted the pseudocapacitive contribution.

SEM showed that PANI nanofibers coated individual graphene sheets uniformly at 10 wt% loading but were confined to the outer surfaces of graphene aggregates at higher loadings. FTIR and XRD confirmed the emeraldine salt phase of PANI and indicated π - π interactions at the PANI-graphene interface. Impedance spectroscopy revealed

the lowest solution resistance (1.82 Ω) for PANI-Gr10, which correlated with the highest capacitance.

These results confirm that moderate graphene loading can substantially enhance both the energy storage capacity and the cycling durability of PANI-based electrodes. Future directions should include asymmetric device assembly using PANI-Gr10 as the positive electrode and activated carbon as the negative electrode, along with testing in gel-polymer electrolytes for flexible supercapacitor applications.

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Contributions Not Qualifying for Authorship

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