Magnetic and Electrochemical Behavior of PANI–Metal Composites and Metal Sulfide Nanoparticles: A Combined Vibrating Sample Magnetometry and Cyclic Voltammetry Study

Nidhi V. Nalkande[1], R P.Pawar[2], Gopalkrushna H. Murhekar[3]

[1,2,3]*Department of Chemistry, Organic Synthesis Division, Government Vidarbha Institute of Science and Humanities Amravati MS, INDIA*

***Abstract*—Magnetic and electrochemical characterization of nanostructured materials provides critical insight into their suitability for advanced technological applications. In this work, polyaniline (PANI), PANI–metal composites (PANI–Cd, PANI–Cu, PANI–Ni), and metal sulfide nanoparticles (CdS, CuS, NiS) synthesized at different precursor concentrations were systematically investigated using Vibrating Sample Magnetometry (VSM) and Cyclic Voltammetry (CV). VSM measurements in an applied field of ±15,000 Oe revealed weak ferromagnetic to paramagnetic behaviour with composition-dependent magnetization. Incorporation of metal ions into PANI significantly enhanced magnetization, with PANI–Ni exhibiting the highest magnetic moment among the composites. Metal sulfide nanoparticles displayed higher magnetization than pristine PANI, and an increase in precursor concentration (0.4–1.0 M) for CdS and NiS led to improved magnetization, suggesting better crystallinity and reduced surface spin disorder. CV studies, performed in the potential window −0.2 to +1.0 V (vs. Ag/AgCl) at 50 mV s^{-1}, demonstrated distinct redox features and pseudocapacitive behaviour. PANI showed two classical redox couples, while PANI–metal systems exhibited higher peak currents, lower peak separations (ΔEp), and increased specific capacitance, confirming enhanced electron transfer and charge storage. Among all samples, NiS and PANI–Ni delivered the highest peak currents, lowest ΔEp, and maximum specific capacitance (160 and 140 F g^{-1}, respectively). The combined VSM–CV analysis highlights a strong structure–property correlation and identifies Ni-based systems as promising candidates for multifunctional applications in supercapacitors, magnetic sensing, catalysis, and magnetic–electrochemical devices.**

***Index Terms*—Polyaniline, Metal sulfide nanoparticles, VSM, Cyclic voltammetry, Magnetization, Specific capacitance, NiS, PANI–Ni.**

I. INTRODUCTION

Conducting polymer–based nanocomposites have emerged as versatile materials for next-generation energy, sensing, and electronic applications owing to their tenable electrical, magnetic, and electrochemical properties. [1-5] Among them, polyaniline (PANI) is particularly attractive due to its environmental stability, facile synthesis, reversible redox behaviour, and controllable conductivity through doping. The integration of transition metals or metal sulphides with PANI further introduces localized magnetic moments, enhanced redox activity, and improved charge transport, thereby enabling multifunctional performance in a single material platform [6-10]. Metal sulphides such as CdS, CuS, and NiS are well-known semiconducting nanomaterials, exhibiting size-dependent optical and electronic properties, mixed ionic–electronic conduction, and defect-induced magnetic ordering at the nanoscale [11-15].

Their coupling with PANI can generate synergistic interactions, giving rise to improved magnetization, redox kinetics, and pseudocapacitive charge storage, which are highly desirable for supercapacitors, sensors, antibacterial coatings, catalysis, and electromagnetic interference (EMI) shielding devices [16-20]. A number of studies have reported the intriguing magnetoelectric and multiferroic behaviour of metal oxide and chalcogenide systems in combination with functional polymers and complex oxides [21-30]. To rationally design such hybrid materials, it is essential to understand the correlation between structure, magnetic response, and electrochemical behaviour. Vibrating Sample Magnetometry (VSM) provides quantitative information on saturation magnetization (Ms), remanent magnetization (Mr), coercivity (Hc), and domain behaviour, while Cyclic Voltammetry (CV) probes redox processes, charge-transfer kinetics, and specific capacitance. A combined VSM–CV investigation thus offers a comprehensive picture of spin configuration, electron transport, and energy-storage performance in nanocomposites [30-34].

In this work, we report a detailed VSM and CV study of pristine PANI, PANI–metal composites (PANI–Cd, PANI–Cu, PANI–Ni), and metal sulfide nanoparticles (CdS, CuS, NiS) synthesized at different precursor concentrations. The aim is to (i) evaluate how metal and metal sulfide incorporation alters the magnetic and electrochemical properties of PANI, (ii) establish clear structure–property relationships, and (iii) identify compositions with optimal multifunctional performance.

II. EXPERIMENTAL

PANI, PANI–metal composites, and metal sulfide nanoparticles (CdS, CuS, NiS) were synthesized via chemical oxidative polymerization and suitable wet-chemical routes, as described in detail in the earlier sections of the thesis (synthesis and characterization chapters). Metal sulfide nanoparticles of CdS and NiS were prepared using precursor concentrations of 0.4 M, 0.8 M, and 1.0 M to study the concentration-dependent effects on magnetic and electrochemical properties. VSM measurements were carried out at room temperature under an applied magnetic field range of −15,000 to +15,000 Oe. Magnetization (M) as a function of magnetic field (H) was recorded, and parameters such as Ms, Mr, Hc, and squareness ratio (Mr/Ms) were extracted from the M–H hysteresis loops.

Electrochemical measurements were performed using a three-electrode configuration with Ag/AgCl as reference electrode, platinum wire as counter electrode, and the synthesized material coated on a suitable current collector as working electrode. CV curves were recorded in the potential window −0.2 to +1.0 V at a scan rate of 50 mV s^{-1}. Peak currents ($I_{p,a}$ and $I_{p,c}$), peak potential separation (ΔEp), integrated charge (Q), and specific capacitance (Csp) were evaluated from the CV responses.

3. Results and Discussion

3.1 Vibrating Sample Magnetometry (VSM) Analysis

The magnetic behaviour of PANI, PANI–metal composites, and metal sulfide nanoparticles was examined using VSM in the field range −15,000 to +15,000 Oe. The representative M–H curves (Figure 1) exhibit narrow hysteresis loops with low remanence and coercivity, characteristic of weak ferromagnetic or predominantly paramagnetic systems with minor ferromagnetic contributions. Table 1 summarizes the calculated and observed magnetization values for all samples.

S. No.	Sample	Calculated M (emu g^{-1})	Observed M (emu g^{-1})
1	PANI	0.30	0.25
2	PANI–Cd	0.50	0.48
3	PANI–Cu	0.70	0.65
4	PANI–Ni	0.80	0.73
5	CdS	0.90	0.87
6	CuS	0.80	0.81
7	NiS	0.85	0.86
8	0.4 M CdS	0.91	0.90
9	0.8 M CdS	0.93	0.94
10	1.0 M CdS	0.94	0.93
11	0.4 M NiS	0.86	0.87

12	0.8 M NiS	0.87	0.88
13	1.0 M NiS	0.90	0.92

Table 1. Observed and calculated magnetization of synthesized PANI-based composites and metal sulfide nanoparticles.

Pristine PANI exhibits the lowest magnetization (0.25 emu g^{-1}), consistent with its weak intrinsic magnetic character dominated by polarons and bipolarons generated upon doping. Upon incorporation of metal ions (Cd^{2+}, Cu^{2+}, Ni^{2+}) into the PANI matrix, a systematic increase in magnetization is observed (PANI < PANI–Cd < PANI–Cu < PANI–Ni). This enhancement arises from localized magnetic moments introduced by metal centres and their interaction with the conjugated polymer backbone, which promotes spin–charge coupling and partial magnetic ordering. Among the composites, PANI–Ni displays the highest magnetization (0.73 emu g^{-1}), indicating stronger metal–polymer coupling and more effective spin alignment. Metal sulfide nanoparticles (CdS, CuS, NiS) exhibit higher magnetization than pristine PANI, confirming the formation of nanoscale domains with exchange-coupled spins and defect-induced magnetic moments. The presence of sulfur vacancies and surface spin disorder at the nanoscale can induce magnetic ordering not observed in bulk counterparts. A clear concentration-dependent behaviour is evident for CdS and NiS: increasing precursor concentration from 0.4 M to 1.0 M leads to a gradual increase in magnetization (0.90 → 0.93 emu g^{-1} for CdS; 0.87 → 0.92 emu g^{-1} for NiS). This trend suggests improved crystallinity, reduction in surface strain, and enhanced spin alignment at higher concentration and better controlled nucleation.

The narrow hysteresis loops with low coercivity and small Mr values indicate predominantly soft magnetic nature or superparamagnetic tendencies in the nanomaterials. The coexistence of paramagnetic and weak ferromagnetic contributions, inferred from loop shape and theoretical fitting, points toward mixed magnetic ordering arising from a combination of single-domain and multi-domain particles. Overall, the VSM results confirm that metal and metal sulfide incorporation markedly improves the magnetic response of PANI-based systems, with Ni-containing materials showing the most promising behaviour for magnetic sensing, data storage, and multifunctional device applications.

3.2 Cyclic Voltammetry (CV) Analysis

CV measurements were conducted to elucidate the redox behaviour, electron-transfer kinetics, and charge-storage capability of the synthesized materials. All measurements were performed in the potential window −0.2 to +1.0 V (vs. Ag/AgCl) at a scan rate of 50 mV s^{-1}. Pristine PANI exhibited two prominent redox couples corresponding to the leucoemeraldine ↔ emeraldine and emeraldine ↔per nigraniline transitions. The first oxidation peak appeared around 0.22–0.30 V, while the second broader oxidation feature was observed near 0.65–0.72 V, confirming the classical proton-coupled electron-transfer mechanism of conducting polyaniline. Incorporation of metal ions into PANI significantly altered the CV profiles. PANI–Cd, PANI–Cu, and PANI–Ni displayed sharper and more intense redox peaks with increased peak currents (Ip) and reduced peak-to-peak separations (ΔEp), indicating improved electron mobility, enhanced electroactive surface area, and better redox reversibility due to synergistic polymer–metal interactions. Among these, PANI–Ni showed the highest anodic peak current and the smallest ΔEp, reflecting superior electron transport and faster redox kinetics. Metal sulfide nanoparticles exhibited broad pseudocapacitive features rather than sharp redox peaks. NiS, in particular, showed a strong, quasi-rectangular CV profile with well-defined anodic and cathodic humps, typical of surface-controlled pseudocapacitive behaviour and efficient charge storage at the electrode–electrolyte interface. The peak assignments and observed electrochemical behaviour are summarized in Table 2.

Sample	Anodic Peak (V)	Cathodic Peak (V)	Assigned Redox Transition	Observed Behavior

PANI	0.28 / 0.70	0.19 / 0.58	LE ↔ ES, ES ↔ PN transitions	Reversible, moderate peak current
PANI–Cd	0.25 / 0.66	0.17 / 0.53	Cd-assisted proton transfer	Slightly improved reversibility
PANI–Cu	0.23 / 0.63	0.15 / 0.49	Cu-facilitated electron hopping	Higher redox current, lower ΔEp
PANI–Ni	0.21 / 0.60	0.12 / 0.44	Ni-induced charge delocalization	Highest redox activity, enhanced kinetics
CdS	0.42	0.31	Cd^{2+}/Cd^{+} surface redox	Weak, broad peak, diffusion-controlled
CuS	0.35	0.26	Cu^{2+}/Cu^{+} reversible redox	Higher current than CdS
NiS	0.30	0.20	Ni^{3+}/Ni^{2+} pseudocapacitive transition	Strongest, most reversible redox/pseudocapacitive response

Table 2. Peak assignment and electrochemical characteristics from CV data.

The CV responses can be summarized as follows:

- PANI: Two sharp, well-defined redox peaks confirm classical conducting polymer behavior with moderate Ip and ΔEp.
- PANI–metal composites: Enhanced peak currents and reduced ΔEp indicate improved ion diffusion, faster charge transfer, and better reversibility due to strong metal–polymer interactions.
- Metal sulfides: Broad, capacitor-like humps demonstrate dominant pseudocapacitive behavior with surface-controlled charge storage.
- Ni-based systems (PANI–Ni and NiS): Larger enclosed area under the CV curves indicates higher charge storage capacity and rapid electrochemical switching. Quantitative electrochemical parameters—Ip,a, Ip,c, ΔEp, integrated charge (Q), and specific capacitance (Csp)—are presented in Table 3.

S. No.	Sample	Ip,a (mA)	Ip,c (mA)	ΔEp (V)	Q (C)	Csp (F g^{-1})
1	PANI	0.45	0.40	0.09	1.8×10^{-4}	72
2	PANI–Cd	0.60	0.56	0.08	2.2×10^{-4}	88
3	PANI–Cu	0.82	0.78	0.07	2.8×10^{-4}	112
4	PANI–Ni	1.05	1.00	0.06	3.5×10^{-4}	140
5	CdS	0.52	0.49	0.10	2.0×10^{-4}	80
6	CuS	0.88	0.83	0.08	3.0×10^{-4}	120
7	NiS	1.20	1.15	0.05	4.0×10^{-4}	160

Table 3. Electrochemical parameters calculated from CV curves.

The incorporation of metal ions into PANI clearly enhances the electrochemical performance. The trend in specific capacitance: NiS (160 F g^{-1}) > PANI–Ni (140 F g^{-1}) > CuS (120 F g^{-1}) > PANI–Cu (112 F g^{-1}) > PANI–Cd (88 F g^{-1}) > CdS (80 F g^{-1}) > PANI (72 F g^{-1}) demonstrates the synergistic contribution of both metallic species and sulfide phases in boosting charge storage capabilities. The smallest ΔEp values for PANI–Ni (0.06 V) and NiS (0.05 V) confirm superior electrochemical reversibility and rapid electron-transfer processes. Scan-rate studies (not shown here) further support diffusion-controlled Faradaic behaviour with pseudocapacitive contributions, particularly for NiS.

3.3 Correlation Between Magnetic and Electrochemical Properties

The combined analysis of VSM and CV results reveals a strong correlation between magnetic ordering, electron transport, and charge-storage behaviour in the synthesized systems.

- Enhanced magnetization in PANI–metal composites and metal sulfides is associated with improved structural ordering, effective metal incorporation, and nanoscale domain formation.

- The same metal incorporation simultaneously introduces additional electroactive centers and facilitates more efficient electron pathways, leading to higher peak currents, lower ΔEp, and greater specific capacitance.
- Ni-based materials, especially PANI–Ni and NiS, consistently show superior performance in both magnetic and electrochemical measurements, indicating that Ni^{2+}/Ni^{3+} redox chemistry and its strong interaction with the PANI backbone are particularly favourable for multifunctional behaviour.

These correlations suggest that rational control of composition, crystal structure, and nanostructure size can be used to tailor both magnetic and electrochemical properties, which is vital for designing materials for supercapacitors, smart sensors, magneto-electronic devices, and EMI shielding applications.

III. CONCLUSIONS

PANI, PANI–metal composites (PANI–Cd, PANI–Cu, PANI–Ni), and metal sulfide nanoparticles (CdS, CuS, NiS) synthesized at varying precursor concentrations were systematically studied using Vibrating Sample Magnetometry and Cyclic Voltammetry. The main conclusions are: Pristine PANI exhibits weak magnetization, whereas incorporation of Cd, Cu, and Ni markedly enhances the magnetic response. Metal sulfide nanoparticles show higher magnetization than PANI, with concentration-dependent enhancement for CdS and NiS, indicating better crystallinity and spin alignment at higher precursor concentrations. The materials display mixed paramagnetic–weak ferromagnetic behaviour with soft magnetic characteristics, suitable for magnetic sensing and multifunctional applications. PANI shows classical two-step redox transitions, while PANI–metal composites and metal sulfides exhibit enhanced redox currents and pronounced pseudocapacitive responses. PANI–Ni and NiS display the highest peak currents, minimum ΔEp, and maximum specific capacitance, confirming superior electrochemical reversibility and charge-storage capability. The synergy between conducting PANI matrix and embedded metal/metal sulfide phases leads to concurrent improvement in magnetic and electrochemical performance. Ni-based systems emerge as the most promising candidates for high-performance supercapacitors, magnetic–electrochemical devices, and other multifunctional applications. Overall, the combined VSM and CV study demonstrates that controlled incorporation of metal and metal sulfide nanoparticles into PANI provides an effective strategy for designing multifunctional nanocomposite materials with tunable magnetic and electrochemical properties.

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