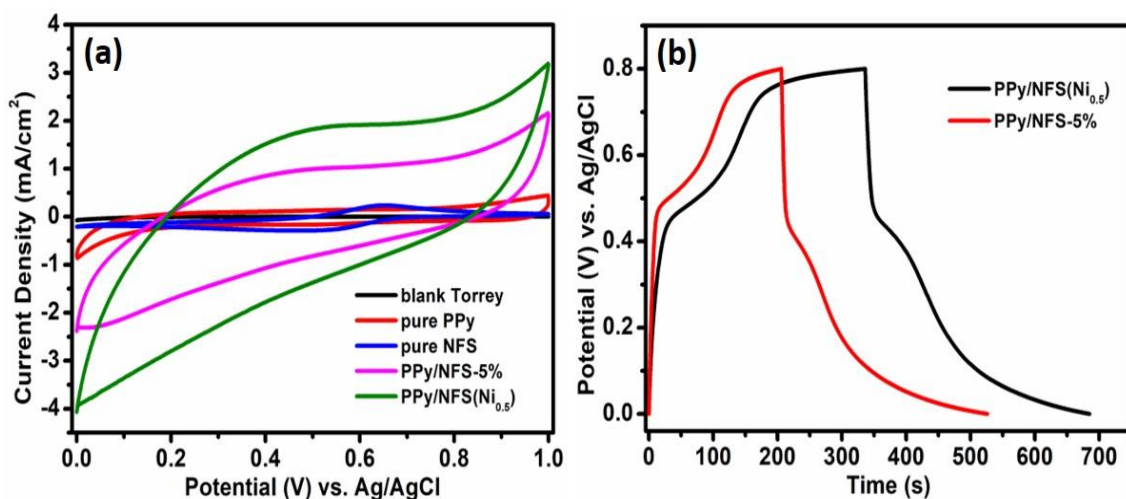


Chapter 6

Investigation of Redox mediated Super capacitive property of PPy/NFS and PPy/Ni-doped NFS composites



This chapter deals with the charge storage property of PPy/NFS and PPy/Ni-doped NFS composites as a supercapacitor. The electrochemical results show that the composites have good charge storage capacity and can be a promising candidate for supercapacitor application.

6.1 Introduction

Energy storage is currently one of the world's biggest challenges due to environmental issues, the energy crisis, and the continuously rising global energy consumption, particularly the quickly expanding market for portable electronic devices like cell phones, laptops and electric vehicles. Researchers put a lot of emphasis on environmentally friendly energy storage and conversion technologies that can better utilize alternative sustainable energies (solar, tide and wind) to meet modern society's needs and address rising environmental concerns [209]. Currently, popular energy storage systems are lead-acid batteries, fuel cells, lithium-ion batteries (LIBs), dissolved redox flow (DRF) and electrochemical capacitors (ECs). They are clean energy-focused electrochemical energy storage technologies [210]. In light of this, ECs, also known as ultra-capacitors, are rapidly replacing traditional capacitors as the electronics sector's primary energy storage technology. They are popular energy storage technologies that offer better capacitance than conventional capacitors (between 100 and 1000 F), lower internal resistance, a longer lifespan, lighter weight, higher efficiency, exceptional cycle stability, ease of production, etc. [210]. With various applications spanning from low to high energy and power requirements, electrochemical capacitor devices have better chances of advancing the next generation of the electronics industry. Additionally, this technology addresses applications that need a larger current to be delivered over a shorter period with many charging and discharging cycles [211]. The Ragone is a crucial diagram illustrating how specific energy and power are distributed among various energy storage systems [210], [212]. Electrochemical capacitors are the best energy storage options for filling the gap between batteries and conventional capacitors. It was discovered that LIBs and ECs have outstanding electrochemical properties, placing them in the front row [209].

The selection of innovative electrode active materials is crucial for developing high-performance ECs to improve electrochemical performance. Priority should be given to materials that are non-toxic, have a narrow bandgap, are ecologically acceptable materials, have supreme electroactive sites, have a greater specific surface area, regulated porosity, have high electrical conductivity, and have good chemical as well as thermal stability [213]. In this context, CPs-based composites with various nanomaterials, such as metals, perovskites, oxides, spinels, di-chalcogenides, hydroxides, MXenes (2D inorganic compounds consisting of atomically thin layered of transition metal carbides, nitrides or carbonitrides), etc., can be thoroughly studied for a wide range of applications [213], [175]. Research on CP-based electrode materials has dramatically improved in recent years to develop efficient electrochemical supercapacitors. However, because of their unique characteristics compared to metal oxides and mesoporous carbon-based materials like CNTs, CPs such as PANI, PPy, and PTh and their derivatives are widely studied by many researchers for electrochemical charge storage applications [70], [175], [214]. Despite this, CPs are used as pseudocapacitive materials due to their exceptional qualities, including their good electrical conductivity, reversible faradic redox nature, rapid doping-dedoping capability, high charge density, fast chemical kinetics, flexibility, tunable morphology, larger surface area, lower cost, and ease of synthesis compared to metal oxides [215]. However, despite their many benefits, using pristine CPs exclusively has drawbacks. For example, structural damage (swelling/shrinking) caused by the charging and discharging process can seriously impair the performance of electrochemical capacitors' rate capability and cyclic stability [216]. Because of this, it has been discovered that composites of CPs with carbon materials [217], metal oxides [21], and transition metal dichalcogenide [218], are excellent for enhancing performance and cyclic stability due to synergistic effects. CP-based supercapacitors are helpful for connecting high-power density with regenerative braking when

frequent stops and short-term acceleration are needed. They can also be used to control battery fluctuations in electric vehicles due to their distinctive energy storage capabilities [210].

In this chapter, low-cost, noble metal-free PPy/NFS and PPy/Ni-doped NFS composites were synthesized via in-situ chemical polymerization. Here, nano NFS and Ni-doped NFS were incorporated into a fixed amount of Py monomer, and polymerization was done using ammonium persulfate as an oxidizing agent. The synthesis of composites was confirmed by structural characterization like XRD. After that, it was characterized for morphological illustrations using SEM and surface area analysis using BET (also refer to chapters 4 and 5). After the structural confirmation of the composites, it was investigated for electrochemical supercapacitor application. The as-synthesized PPy/NFS-5% composite (optimized ratio for NFS) shows good charge storage properties and displays the specific capacitance (C_{sp}) of 438 F/g. The PPy/Ni-doped NFS($Ni_{0.5}$) composite (optimized ratio for Ni doping in NFS) offers a better charge storage property and has a specific capacitance value of 562 F/g.

6.2 Experimental section

Materials: Mohr's salt (Sigma Aldrich, $\geq 99\%$), sodium carbonate (Sigma Aldrich, $\geq 99.5\%$), sodium hydrogen phosphate (Merck, $\geq 99\%$), Nickel sulfate (Merck, $\geq 98\%$), Pyrrole monomer (Sigma Aldrich), ammonium persulphate (Merck, $\geq 98\%$).

Synthesis of NFS and Ni-doped NFS

The synthesis of NFS and Ni-doped NFS was done by simple co-precipitation method as follows (refer to chapters 4 and 5): 7.92 g of Mohr's salt was dissolved in 100 ml of DI water under stirring conditions followed by the addition of sodium hydrogen phosphate with further stirring for 2 hours at 90°C to mix them properly. Then, 1.07 g of sodium carbonate was added to the above solution mixture, which spontaneously caused the evolution of CO_2 . Ammonia

solution was then added for precipitation under basic conditions. It was then dried and calcinated at 500° C to get crystalline NFS.

Ni-doped NFS was synthesized in a similar co-precipitation method by adding 0.5 M nickel sulfate to the above reaction mixture before adding sodium carbonate.

Synthesis of PPy-NFS and PPy-Ni-doped NFS

The synthesis of PPy/NFS and PPy/Ni-doped NFS was done by the oxidative chemical polymerization method (refer to chapters 4 and 5). Initially, the as-synthesized nanoparticle of NFS was mixed with Py monomer in 70 ml of DI water for proper mixing. After that, 30 ml of 100 mM APS solution was added to it slowly dropwise for polymerization under constant stirring. The reaction mixture was left as such for one day to complete polymerization. The next day it was washed, filtered, and dried for characterization.

PPy/NFS(Ni) was synthesized similarly by taking Ni-doped NFS instead of NFS.

Electrode fabrication

First, a slurry ink was prepared by dispersing 4 mg of composites into 1 ml of water-ethanol (3:2 ratio) mixture. It was then ultra-sonicated for exfoliation and to better dispersion on the electrode. It was cast on Torrey paper, having a unit area. The modified Torrey paper electrode was dried at 60° C in a vacuum oven. It was then used as an active electrode material for supercapacitor application.

6.3 Results and discussion

Structural analysis

The crystal structure and phases of as-synthesized materials have been investigated through the X-ray diffraction technique. The XRD pattern of the as-synthesized composite materials is

shown in figure 6.1. The XRD analysis confirms the rhombohedral phase of NFS, NFS(Ni) in PPy/NFS, and PPy/NFS(Ni_{0.5}) composites, respectively [171]. As shown in Figure 6.1(a), pure NFS exhibits a rhombohedral phase with space group ' $R\bar{3}c$ ', while varying the Ni doping concentration in pure NFS, did not cause any phase change except for some lattice defects. PPy shows a broad, amorphous type XRD pattern that is well-matched [174]. In composites, there can be seen some diffraction peaks over the amorphous background of PPy, and these peaks correspond to crystalline NFS and NFS-Ni_{0.5}, respectively. Thus, XRD patterns evidenced the successful synthesis of PPy, NFS, Ni-doped NFS, and their composites.

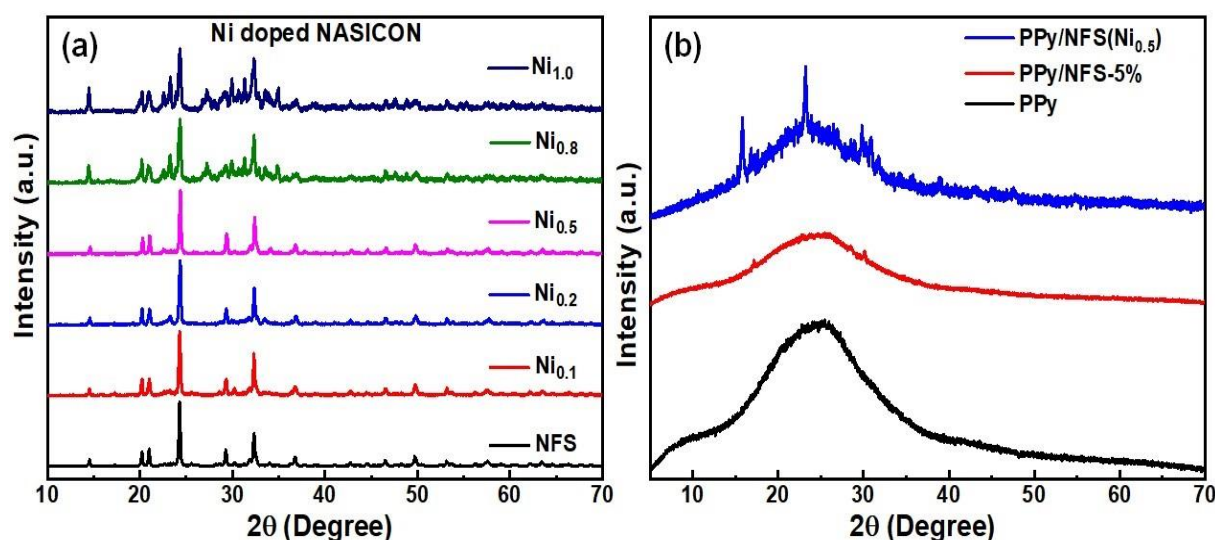


Figure 6.1: (a) XRD spectra of pure NFS and NFS(Ni_x) with different Ni doping, (b) The XRD pattern of pristine PPy, PPy/NFS-5% and PPy/NFS(Ni_{0.5}) composites.

Morphological analysis

The morphological investigation of as-synthesized composite materials has been done using SEM. The SEM and mapping ensure the excellent incorporation of NFS into the PPy matrix (figure 6.2). The morphology of polypyrrole is spherical (figure 6.2a), while that of NASICON structure ($\text{Na}_3\text{Fe}_2(\text{SO}_4)_2(\text{PO}_4)$) is irregular granule-like (figure 6.2b). The PPy/NFS-5% (optimized ratio) (figure 6.2c) shows a spherical morphology with a smaller diameter than pure

PPy. The morphology of Ni-doped NFS (NFS-Ni) is also irregular granule-like with some particle-like, giving mixed morphology (figure 6.2d). The composite so formed from PPy and NFS-Ni, i.e. (PPy/NFS(Ni_{0.5})) (figure 6.2e), is spherical, having a small size than pure PPy and PPy/NFS-5% and hence provides more surface area and therefore more electrocatalytic active sites. The mapping (figure 6.2f) shows the uniform distribution of different elements present in the composites.

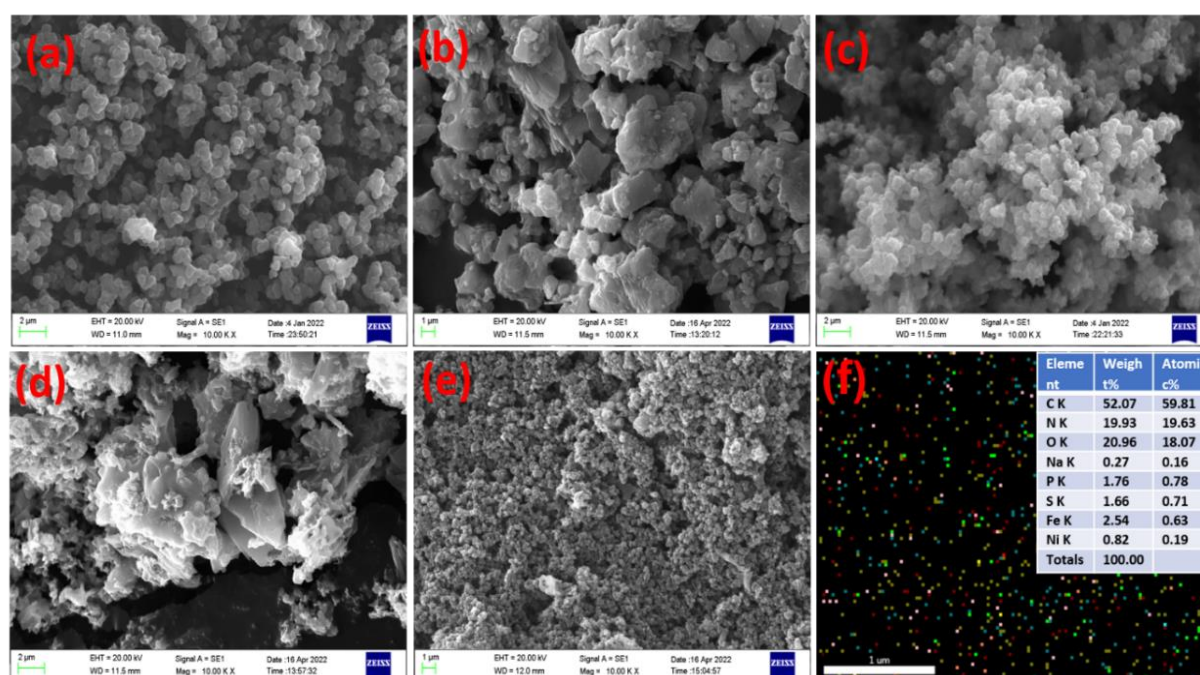


Figure 6.2: SEM image of (a) pristine PPy, (b) NFS pure, (c) composite PPy/NFS-5%, (d) NFS(Ni_{0.5}) (optimized ratio for Ni), (e) composite PPy/NFS(Ni_{0.5}) and (f) elemental mapping of PPy/NFS(Ni_{0.5}).

Electrochemical analysis

The charge storage property of the synthesized composite materials is investigated using Cyclic voltammetry (CV). The typical CV curve of pristine PPy, pure NFS and blank Torrey paper, along with PPy/NFS composites, are displayed in figure 6.3(a). Figure 6.3(b) represents the cyclic voltammogram of PPy/NFS-5% and blank Torrey, pure PPy, and pure NFS for

comparison purposes. The CV depicted in Figure 6.3 is performed in an aqueous medium using 0.5 M H₂SO₄ as an electrolyte in a three-electrode system from 0 to 1 V of the potential window. The materials loaded on the working electrode weigh 1 mg/cm². The specific capacitance (C_{sp}) for composite materials is calculated using the area under the CV curve with the help of the formula shown below.

$$C_{sp} = 1/(mv\Delta V) * \int i.dV \quad (\text{eq. 1.17})$$

where C_{sp} is the specific capacitance

The values of specific capacitance calculated using the above formula are depicted in figure 6.3(d). The specific capacitance for pure PPy, pure NFS, and composite PPy/NFS-5% are 162.5 F/g, 95 F/g, and 438.37 F/g, respectively, at the scan rate of 10 mV/s. The shape of the CV curve is nearly rectangular and symmetrical along the zero current axis with partially oxidation-reduction peaks in composite materials showing a pseudocapacitor [210], [6], [70]. The drastic increase in the specific capacitance values of composite materials PPy/NFS-5% is due to the optimized synergistic effect between the PPy and pure NFS. It may also be due to high pseudocapacitance, and high specific surface area implies the enhanced availability of redox-active sites generated due to the incorporation of NFS. A small amount of NFS in the polymer matrix can improve the electrochemical activity by many folds, which can be seen in the CV. Figure 6.3(c) depicts the cyclic voltammogram of PPy/NFS-5% at various scan rates ranging from 10 mV/s to 200 mV/s and their change in the specific capacitance is plotted in Figure 6.3(d). It can also be seen that with the increase in scan rates, the value of specific capacitance decreases, as per the formula above.

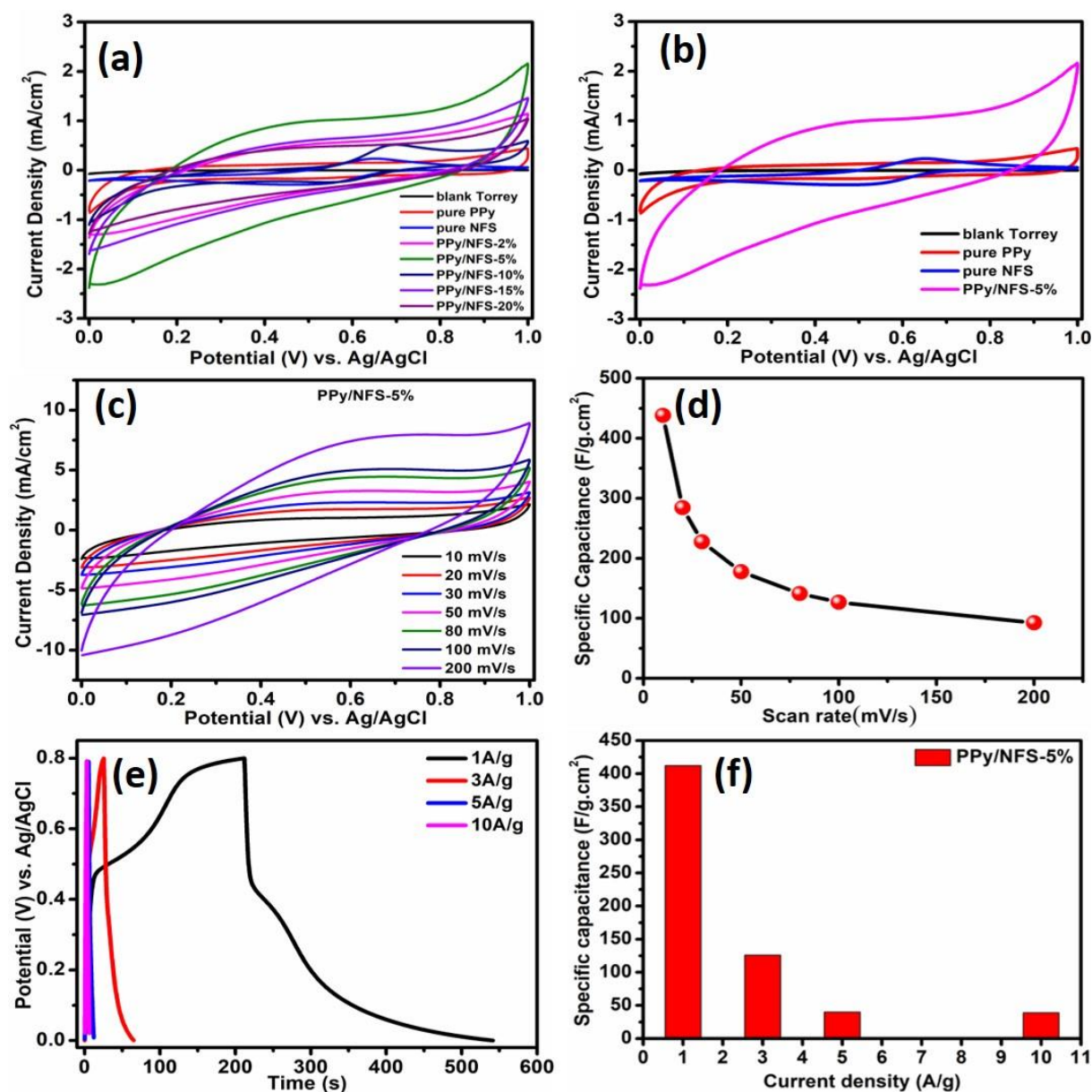
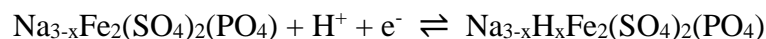


Figure 6.3: (a) The CV curve of pure PPy, pure NFS, and PPy/NFS composites, (b) CV curve of PPy/NFS-5% with pure PPy and pure NFS, (c) CV of PPy/NFS-5% at the different scan rates, and (d) corresponding specific capacitance, (e) Galvanic charge-discharge (GCD) of PPy/NFS-5% at different current density, (f) specific capacitance corresponding to GCD at different current densities. The electrolyte used here is 0.5 M H₂SO₄ solution.

Further, the determination of the specific capacitance of composites PPy-NFS-5% is carried out using the galvanic charge-discharge (GCD) method, as shown in figure 6.3(e). It shows the CD curve at the current densities ranging from 1 A/g to 10 A/g. The asymmetrical triangular curve

with inadequate charge transfer resistance during charging-discharging, even at very high current densities having a low ohmic drop, indicates a very high rate of performance [219], [175]. The discharging time is more than the charging time, as seen from the potential-time profile of the CD curve, indicating the good capacitive performance of the electrode materials. The specific capacitances calculated from the GCD curve (using eq. 1.18) are 412.3 F/g, 126 F/g, 40 F/g, and 39 F/g, corresponding to current densities of 1 A/g, 3 A/g, 5A/g, and 10 A/g, respectively which are depicted in the bar graph in Figure 6.3(f). The GCD (figure 6.3(e)) curves clearly demonstrate the process is diffusion controlled as we observed transitions during charging-discharging. This is because, during the charging and discharging, the H⁺ ion from the electrolytes intercalated/de-intercalated in the lattice of sodium of NFS and the following reaction takes place at the electrode-electrolyte interface.



In composite PPy/NFS-5%, the Faradic process from the NFS part contributes to the overall capacitance value and enhances the total specific capacitance of the composite. It could be concluded that the composite materials have good potential for supercapacitor application and excellent stability.

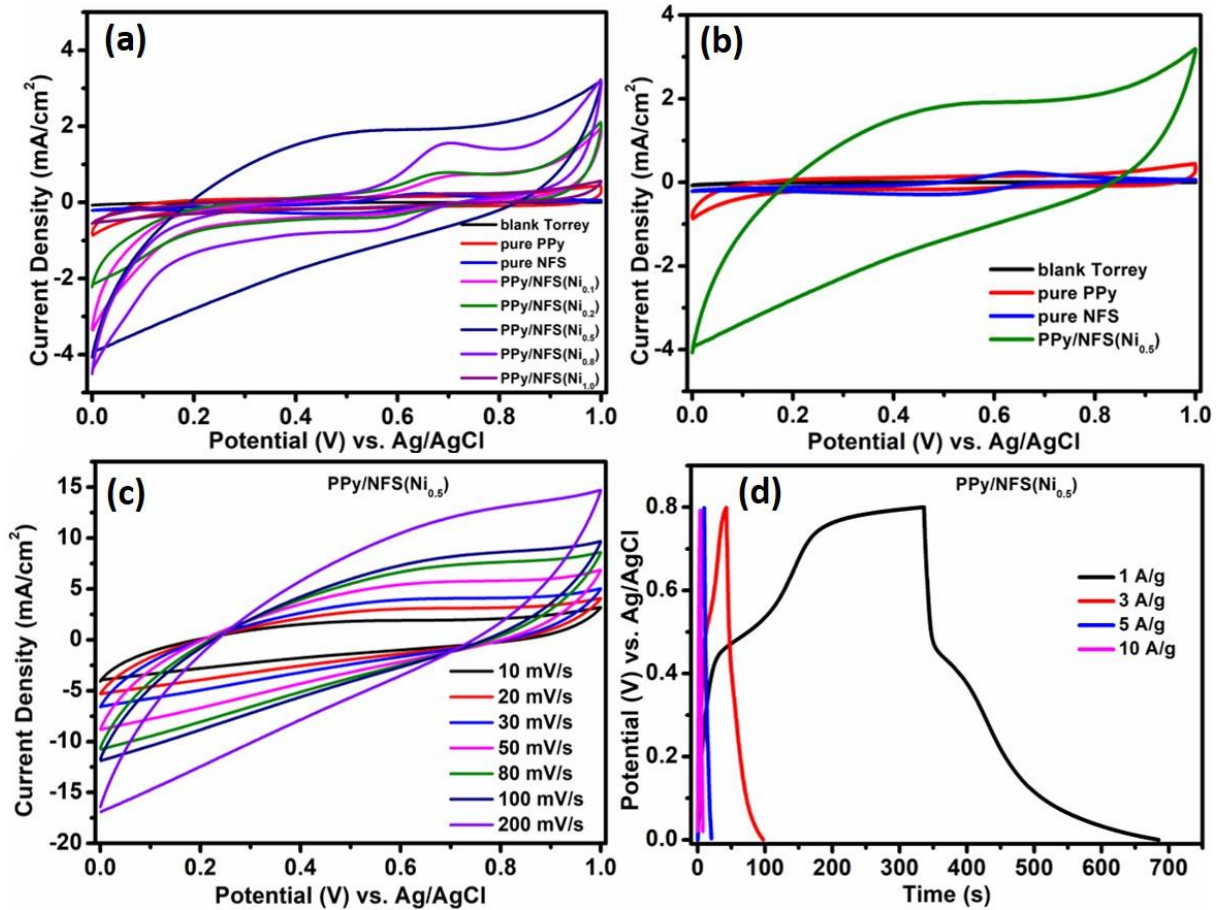


Figure 6.4: (a) CV curve of blank Torrey paper, pure PPy, pure NFS and various PPy/NFS(Ni_x) composites, (b) CV of PPy/NFS(Ni_{0.5}) with pure PPy and pure NFS for comparison, (c) CV at different scan rates and (d) GCD curve of PPy/NFS(Ni_{0.5}) at different current densities. The electrolyte used here is 0.5 M H₂SO₄ solution.

The electrochemical charge storage property of various ratios of composites PPy/NFS(Ni_x) is also investigated using CV and GCD curves, as displayed in figure 6.4. The CV curve of different PPy/NFS(Ni_x) composites and pure PPy and pure NFS are plotted in figure 6.4(a). It can be seen from figure 6.4(a) the PPy/NFS(Ni_{0.5}) has a higher CV curve area indicating charge storage capacity compared to the other ratios and pure PPy and NFS. Figure 6.4(b) shows the CV curve of PPy/NFS(Ni_{0.5}) with pure PPy and NFS for comparison purposes. The specific capacitance of pure PPy, pure NFS, and composite PPy/NFS(Ni_{0.5}) (optimized ratio for Ni) are 162.5 F/g, 95 F/g, and 562 F/g, respectively, at the scan rate of 10 mV/s. The dramatic increase

in the specific capacitance values of composite materials PPy/NFS(Ni_{0.5}) is due to the optimized synergistic effect between the PPy and pure Ni-doped NFS. It may also be due high specific surface area implies the enhanced availability of redox-active sites generated due to the incorporation of Ni-doped NFS (refer to chapter 5). A small amount of Ni doping into NFS increases redox-active sites [220]. Therefore, the small incorporation of Ni-doped NFS into the polymer matrix can enhance the electrochemical charge storage performance by many folds, which can be seen in the CV curve. The effect of scan rate on the specific capacitance of PPy/NFS(Ni_{0.5}) was investigated and shown in figure 6.4(c). The value of C_{sp} decreases as the scan rate increases.

Further, the determination of C_{sp} of composites PPy/NFS(Ni_{0.5}) is carried out using the galvanic charge-discharge (GCD) method, as shown in figure 6.4(d). It shows the CD curve at the current densities ranging from 1 A/g to 10 A/g. The specific capacitances of PPy/NFS(Ni_{0.5}) calculated from the GCD curve (using eq. 1.18) are 521 F/g, 239 F/g, 142 F/g, and 121 F/g, corresponding to current densities of 1 A/g, 3 A/g, 5A/g, and 10 A/g, respectively which are depicted in the bar graph in Figure 6.3(f). The PPy/NFS(Ni_{0.5}) shows a pseudocapacitive behavior, as seen from CV and GCD curves. Incorporating Ni into NFS enhanced the redox-active sites and improved the charge storage capability in PPy/NFS(Ni_{0.5}) composites. The EIS data from chapters 4 and 5 supports the better electrochemical performance of PPy/NFS and PPy/NFS(Ni_{0.5}) composites, as the charge transfer resistance is minimal in these cases.

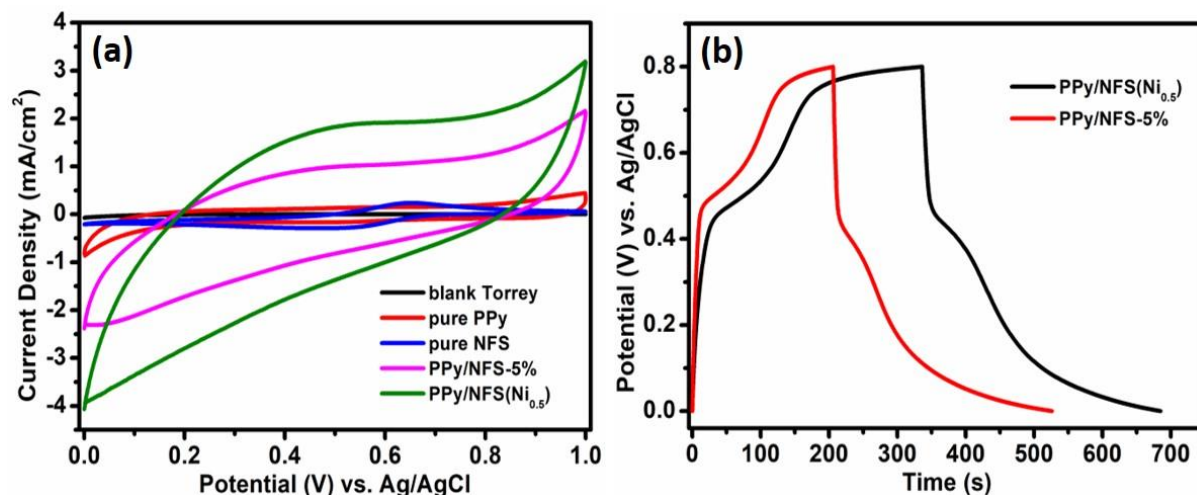


Figure 6.5: (a) Comparison of C_{sp} of PPy/NFS-5% and PPy/NFS(Ni_{0.5}) along with pristine PPy and NFS, and (b) GCD curve comparison of PPy/NFS-5% and PPy/NFS(Ni_{0.5}).

The specific capacitance values of PPy/NFS-5% and PPy/NFS(Ni_{0.5}) are shown in figure 6.5 using CV and GCD curves for comparison. In the CV curve (figure 6.5(a)), the higher curve area for PPy/NFS(Ni_{0.5}) than PPy/NFS-5% shows the higher charge storage capacity. The same trend is also observed in the case of the GCD curve, as shown in figure 6.5(b). The reason for the higher C_{sp} value PPy/NFS(Ni_{0.5}) is due to increased active sites for the redox process. The Ni doping in NFS causes the availability of more active sites. The optimized synergistic effect between Ni-doped NFS and PPy in composite PPy/NFS(Ni_{0.5}) enhances the C_{sp} value. Incorporating Ni-doped NFS in the PPy matrix facilitates the ease of charge transfer and accumulation on the surface of active sites. This synergy is optimized in the case of the PPy/NFS(Ni_{0.5}) composites and hence shows better charge storage performance.

6.4 Conclusion

The composites PPy/NFS and PPy/NFS(Ni_{0.5}) are synthesized by the chemical polymerization method. The chemical co-precipitation method was used to synthesize the NFS and NFS(Ni_x), and XRD confirmed their formation. The morphological study and mapping show the spherical shape and uniform distribution of NFS and NFS(Ni_x) in the polymer matrix. The electrochemical study shows that PPy/NFS-5% composite ratio has a higher C_{sp} value of 438 F/g than other PPy/NFS ratios. This is due to the optimized synergic effect between NFS and PPy. The PPy/NFS(Ni_{0.5}) composite shows the highest specific capacitance value than other PPy/NFS(Ni_x) ratios with a C_{sp} value of 562 F/g. The doping of Ni in NFS causes more active sites, and incorporating NFS(Ni_{0.5}) into the polymer matrix creates more electrochemical surface area, which stores more charge. Hence, low-cost, toxic metal-free, environmentally friendly PPy/NFS(Ni_{0.5}) is a promising candidate for efficient supercapacitor performance.