NANOCOMPOSITE MATERIALS FOR HIGH-PERFORMANCE ELECTROCHEMICA SUPERCAPACITORS
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Lay abstract

The rapid increase in human population has caused many economic problems, one of them the enormous energy consumption rate as compared to the limitations of sources available for clean and renewable energy sources.

Energy storage systems can be classified into different types, e.g., chemical, electrochemical, thermal, and mechanical systems. Popular electrochemical energy storage systems, such as batteries and capacitors, are used for many important daily applications but have difficulties while optimizing power and energy densities. Here, electrochemical supercapacitors (ESs) are considered potential energy storage systems that could balance power and energy densities with fast charge-discharge and a long lifetime.

The purpose of this research is to advance nanocomposite materials for electrochemical supercapacitor applications, where we use new colloidal approaches to fabricate high-performance electrochemical supercapacitor electrodes and devices. Our results reveal that these devices can have exceptional performance that facilitates new routes for their development.
Abstract

Electrochemical supercapacitors (ESs) are one of the most modern energy storage systems that offer a balance between power and energy densities in which the energy storage mechanisms could be an electrostatic double layer (EDLCs) and pseudocapacitive.

In this thesis, hybrid asymmetric supercapacitors have been developed to optimize the advantages for different types of (ESs) such as high conductivity, stability, fast charge-discharge, and relatively high performance. These developments include high active mass loading electrodes based on multiwall carbon nanotubes (MWCNTs) and transition metal oxides with incubation of low binder percentage and a high mass loading of 40 mg cm\(^{-2}\) that guarantees high electrochemical performance at a wide potential range for different electrodes, especially the cathodic one. Novel synthesis techniques and different multi-dispersants have been demonstrated; a conception colloidal fabrication method has been developed to improve the morphology/ dispersion for composites of Fe\(_3\)O\(_4\)//MWCNTs (M-CNTs) and NiFe\(_2\)O\(_4\)//MWCNTs.

Firstly, an advanced synthesis method called particle extraction through a liquid-liquid interface (PELLI) has been developed to enhance the dispersion of the nanoparticles M-CNTs. Furthermore, palmitic acid (PA) has been used as a surfactant in the bottom-up (PELLI) to reduce the agglomeration of M-CNTs with high Gamma (\(\gamma\)) ratio (nanoparticles/MWCNTs).
Moreover, different synthesis methods have been developed in the presence of celestine blue dye (CB) as a co-dispersant with advanced electrostatic interaction and coagulation mechanism that ensured well-dispersed of \((\text{Fe}_3\text{O}_4, \text{NiFe}_2\text{O}_4)\) coated (MWCNTs) at high mass loading.

Subsequently, more optimizations have been done to analyze the effect of different adsorption mechanisms by using other co-dispersant agents such as pyrocatechol violet (PV), azure A chloride (AA), and m-cresol purple (CP).

Finally, cyclic voltammetry, galvanic charge-discharge (GCD), electrochemical impedance spectroscopy (EIS), and cyclic stability have been done for the fabricated electrodes and devices in neutral aqueous electrolytes that showed a relevant electrochemical performance in a large potential range.
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M. Nawwar
Declaration of academic achievements

This dissertation was used to fulfill the requirements of an engineering Ph.D. degree. All the research projects were conducted from September 2018 to June 2021. Within this thesis research, advanced colloidal synthesis techniques and constructed materials have been adequately developed to fabricate composites. The developed composites have been suitable for the positive and negative electrodes of ESs. The major contributions of this thesis work were from my supervisors and me. The work of this thesis resulted in four journal papers; all of them were accepted and published in peer-reviewed journals. I was the first author and contributor on these papers that were listed in the following:


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<td>A, mA (unit)</td>
<td>Ampere, milliamp</td>
</tr>
<tr>
<td>AC, ACNTs, AMWCNTs</td>
<td>Activated Carbon nanotubes</td>
</tr>
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<td>C</td>
<td>Capacitance</td>
</tr>
<tr>
<td>C°</td>
<td>Temperature in Celsius</td>
</tr>
<tr>
<td>CCell</td>
<td>Overall cell capacitance</td>
</tr>
<tr>
<td>Cdl</td>
<td>Capacitance from double layer</td>
</tr>
<tr>
<td>C+ve</td>
<td>Capacitance of positive electrode</td>
</tr>
<tr>
<td>C-ve</td>
<td>Capacitance of negative electrode</td>
</tr>
<tr>
<td>CB</td>
<td>Celestine blue dye</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotubes</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry, cyclic voltammogram</td>
</tr>
<tr>
<td>CCP</td>
<td>Chemical co-precipitation</td>
</tr>
<tr>
<td>CP</td>
<td>M-cresol purpule</td>
</tr>
<tr>
<td>C, µC (unit)</td>
<td>Coulomb, micro coulomb</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
</tr>
<tr>
<td>DM-CNT</td>
<td>Dried magnetite carbon nanotubes</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic light scattering</td>
</tr>
<tr>
<td>EDLC</td>
<td>Electrochemical double layer capacitor</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>ESs</td>
<td>Electrochemical supercapacitors</td>
</tr>
<tr>
<td>EM-CNT</td>
<td>Extracted magnetite carbon nanotubes</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>ESR</td>
<td>Equivalent series resistance</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive x-ray spectroscopy</td>
</tr>
<tr>
<td>EPD</td>
<td>Electrophoretic deposition</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Permittivity in vacuum</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>Permittivity between electrodes</td>
</tr>
<tr>
<td>E</td>
<td>Electrode potential</td>
</tr>
<tr>
<td>$E^0$</td>
<td>Standard electrode potential</td>
</tr>
<tr>
<td>$E_{total}$</td>
<td>Total energy stored in a capacitor</td>
</tr>
<tr>
<td>F</td>
<td>Farad, Faraday constant</td>
</tr>
<tr>
<td>FDCNT</td>
<td>Fe$_3$O$_4$–decorated CNT</td>
</tr>
<tr>
<td>$f$</td>
<td>Frequency</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-transform infrared spectroscopy</td>
</tr>
<tr>
<td>g, mg, μg (unit)</td>
<td>Gram, milligram, microgram</td>
</tr>
<tr>
<td>Gamma ($\gamma$)</td>
<td>Relative mass ratio (nanoparticle/MWCNTs)</td>
</tr>
<tr>
<td>h (unit)</td>
<td>Hours</td>
</tr>
<tr>
<td>Hz (unit)</td>
<td>Hertz</td>
</tr>
<tr>
<td>I</td>
<td>Current</td>
</tr>
<tr>
<td>IEP</td>
<td>Isoelectric point</td>
</tr>
<tr>
<td>ILQs</td>
<td>Ionic Liquids</td>
</tr>
<tr>
<td>IHP</td>
<td>Inner Helmholtz plane</td>
</tr>
<tr>
<td>K (unit)</td>
<td>Temperature in Kelvin</td>
</tr>
<tr>
<td>L (unit)</td>
<td>Liter</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>Multi-walled carbon nanotubes</td>
</tr>
<tr>
<td>M-CNTs</td>
<td>Magnetized carbon nanotubes</td>
</tr>
<tr>
<td>MNP</td>
<td>Magnetic nanoparticles (Fe$_3$O$_4$)</td>
</tr>
<tr>
<td>M</td>
<td>Molar concentration</td>
</tr>
<tr>
<td>MOPC</td>
<td>Magnetically ordered pseudocapacitors</td>
</tr>
<tr>
<td>m</td>
<td>Mass of active materials</td>
</tr>
<tr>
<td>m (unit)</td>
<td>Meter</td>
</tr>
<tr>
<td>NPs</td>
<td>Nanoparticles (Fe$_3$O$_4$ or NiFe$_2$O$_4$)</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>OHP</td>
<td>Outer Helmholtz plane</td>
</tr>
<tr>
<td>PELLI</td>
<td>Particle extraction through liquid-liquid interface</td>
</tr>
<tr>
<td>PVB</td>
<td>Polyvinyl butyral</td>
</tr>
<tr>
<td>PM</td>
<td>Physical mixing</td>
</tr>
<tr>
<td>pH</td>
<td>Degree of acidity (-log H⁺)</td>
</tr>
<tr>
<td>PC</td>
<td>Propylene carbonate</td>
</tr>
<tr>
<td>Q</td>
<td>Charge stored</td>
</tr>
<tr>
<td>R</td>
<td>Resistance</td>
</tr>
<tr>
<td>s (unit)</td>
<td>Second</td>
</tr>
<tr>
<td>SCE</td>
<td>Saturated calomel electrode</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium dodecyl sulfate</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>Sp</td>
<td>Power density</td>
</tr>
<tr>
<td>Se</td>
<td>Energy density</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning transmission electron microscope</td>
</tr>
<tr>
<td>SWCNT</td>
<td>Single-walled carbon nanotube</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>TEMABF₄</td>
<td>Triethylmethylammonium tetrafluoroborate</td>
</tr>
<tr>
<td>δM</td>
<td>Relative mass ratio (material/current collector)</td>
</tr>
<tr>
<td>UPD</td>
<td>Under potential deposition</td>
</tr>
<tr>
<td>V (unit)</td>
<td>Volt</td>
</tr>
<tr>
<td>V</td>
<td>Voltage</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>Z</td>
<td>Real part of impedance</td>
</tr>
<tr>
<td>Z'</td>
<td>Imaginary part of impedance</td>
</tr>
</tbody>
</table>
Chapter 1

Literature review

1.1 Introduction

A rapid increase in the human population causes many economic problems; one of them is the enormous rate of energy consumption compared to the limitations of sources. The reason for that could be climate change, pollution, and the depletion of natural energy resources such as fossil fuels [1].

Recently, research and development organizations are trying to discover new economic energy sources and develop efficient mechanisms for the existing energy storage systems [2].

Classifications of the energy storage systems can be divided into chemical, electrochemical, thermal, and mechanical systems [1, 2]. The traditional electrochemical energy storage systems (batteries and capacitors) are used for many daily important applications, like electronic devices, electrical systems, and hybrid vehicles. These traditional systems have some imperfections, such as the large size of the device, operational time limitations, and performance range [2]. Therefore, trying to meet the requirements for future aims, many effective technologies for electrochemical energy storage and conversion systems have become a concern for all developers and inventors, especially the electrochemical supercapacitors with different types, as shown in (Figure 1.1) [3].
The electrochemical supercapacitor (ESs) is one of the modern energy storage systems that offer a balance between power and energy densities, in which the energy storage mechanism depends on one of two main mechanisms; electrostatic double layer (EDLCs) and pseudo capacitance [3]. The classification of the (ESs) can be presented as (EDLCs), Pseudo, and hybrid capacitors depending on the type of the used active materials beside the working mechanism. To optimize (EDLCs) and pseudocapacitor’s advantages, such as high conductivity, stability, and relatively high performance; this research investigates the hybrid asymmetric supercapacitors using different composites/fabrication techniques. These investigations include composites of magnetized carbon nanotubes Fe$_3$O$_4$/MWCNTs (M-CNTs) and nickel ferrite carbon nanotubes NiFe$_2$O$_4$/MWCNTs using different synthesizing methods and a higher mass ratio of (nanoparticles /MWCNTs).
1.2 Fundamentals

Power and energy densities, cyclic stability, and charge-discharge efficiency are considered important parameters that govern an energy storage device’s performance. The relation between power and energy densities vs discharge time is illustrated in the Ragone plot shown in (Figure 1.2) [5].

![Ragone plot for the main energy storage devices, relative discharge time in the dashed line [5].](image)

To further explain fundamentals and different parameters that govern the (ESs), the conventional electrostatic capacitor is shown in (Figure 1.3). It consists of two conductive current collector plates (electrodes), separated by an insulating dielectric plate. Initially, the electrodes are electrically neutral, and at the point of applying the voltage, the polarization
and re-orientation processes happen to the dielectric material where the opposite charges accumulate on the surfaces of each plate and the produced electric field allows the capacitor to store energy [6].

Figure 1.3 Schematic of simple conventional electrostatic capacitor [6].

One of the main advantages of the ideal capacitor is the stability of the capacitance value \( C \) (Farad). This value is defined by the relationship of accumulated charges \( Q \) on a certain electrode and the applied voltage \( V \) between the two electrodes that could be calculated by Eq. 1.1 [7].

\[
Q = C \ V \tag{Eq. 1.1}
\]

Where \( Q \) is the charge stored, \( V \) is the voltage across the plates, and \( C \) is the capacitance of the dielectric capacitor.
For a typical capacitor, \( C \) is proportional to the ratio of the surface area \( A \) of each electrode and the distance between the electrodes \( d \), the proportionality constant is the permittivity and it can be demonstrated as follows:

\[
C = \varepsilon_0 \varepsilon_r \frac{A}{d}
\]  
(Eq. 1.2)

Where \( \varepsilon_0 \) content represents the permittivity of insulating material in the free space (vacuum) (F m\(^{-1}\)) and \( \varepsilon_r \) represents the permittivity of it between the electrodes [7, 8].

Two important parameters can be used to identify the performance of a capacitor, the power and energy values, which can be expressed in the term of specificity (mass/volume) as power and energy densities. Equations 1.3 and 1.4 can express the stored energy \( E \) and power \( P \) of a capacitor and it is obvious that the stored energy depends on the capacitance and the voltage between the plates.

\[
E = \frac{1}{2} CV^2
\]  
(Eq. 1.3)

\[
P = IV = \frac{V^2}{4 \times ESR}
\]  
(Eq.1.4)

An electric circuit with external load resistance \( R \) in series can be used to calculate the power of a capacitor, in addition to internal resistance, depends on various components of the capacitor, such as dielectric material, current collector, and the electrodes, which represented in the form of equivalent series resistance (ESR) [7, 8]. Conventional capacitors have a high power density relative to the electrochemical supercapacitors (ESs), while (ESs) have a much higher energy density that attracts more people’s attention [7, 8].
1.3 **Classifications of electrochemical supercapacitors (ESs)**

Electrochemical supercapacitors (ESs) are one of the modern energy storage systems that offer a balance between power and energy densities. Figure 1.4 shows the classifications of the (ESs), in which the (ESs) can be divided into three main categories electrostatic double-layer (EDLCs), Pseudo, and hybrid capacitors and that is according to the type of active material beside the mechanism of the energy storage. These categories depend on one of the two main mechanisms of storage mechanisms EDLCs / pseudocapacitance or in most cases a combination of them [9].

![Classifications of supercapacitors](image)

Figure 1.4 Classifications of electrochemical supercapacitors (ESs).

According to the nature of the active materials and the mechanism of the energy storage, (ESs) can be classified as symmetric or asymmetric hybrid. The symmetric supercapacitors consist of the same kind of materials or the same mechanism of the energy storage system
and the asymmetric one depends on combinations of different energy storage mechanisms or material types [10].

1.3.1 Electrostatic double layer capacitors (EDLCs)

Electrostatic double-layer capacitors (EDLCs) are the main commercial product of (ESs), in which the storage mechanism relies on the separation of charge in a Helmholtz double layer at the interface between the surface of a current collector electrode and an electrolyte [9]. The most popular (EDLCs) depend on the fabrication of electrodes with an active mass loading of the carbon-based materials, such as carbon nanotubes, graphene, and activated carbon. These porous carbon materials usually have surface areas in the range of 500-3000 m² g⁻¹, and theoretically, these electrodes have theoretical C around 15-50 (μF cm⁻²) or above 500 F g⁻¹ in aqueous electrolytes. However, the obtainable capacitances for carbon-based materials are often below 50 F g⁻¹ due to limited electrolyte access into pores and low electrical conductivity [11].

Despite the small capacitance of these types of active materials, the (EDLCs) mechanism is a neat electrostatic action and there is no phase change, which allowed them to have a remarkably long cyclic life [12]. The dependence on these materials is due to their high surface area, good conductivity, and ability to be functionalized with other materials, in addition to their advantage of enhancing the specific power. Figure 1.5 shows a simple schematic representation for symmetric (EDLCs) of pure carbon-based materials. It consists of a positive and a negative electrode immersed in an electrolyte, which offers a higher capacitance per volume using high surface area porous carbon materials as active materials [11,12].
The charge-discharge mechanism revealed from the pure electrostatic charges accumulation and separation at the electrode/electrolyte interface on both electrodes. Increasing the capacitance resulted from the declination of the potential through an interface layer and hence increasing the charges that are called double layer that is shown in (Figure 1.6) [3, 12].

Figure 1.6 Schematics of EDLC during the charge-discharge cycles [3].

Figure 1.5 Schematic of EDLC [11].
1.3.2 Electrochemical pseudocapacitors

Pseudocapacitors could be considered as the new approach for the development of the commercial products for (ESs) [13], in which the storage of the energy is achieved by a faradaic electron charge-transfer with redox reactions as shown in Figure 1.7 [3,14].

![Figure 1.7 Schematic of mechanisms for pseudocapacitance](image)

The active materials for pseudocapacitors are redox materials with high specific energy storage capacities such as transition metal oxides and conductive polymers. Pseudocapacitors have many advantages, such as relatively higher energy density due to the principle that the faradaic process is normally slower than the non-faradaic process. Another advantage is the efficient cyclic stability and the poses of a fast charge-discharge cycle that makes them convenient for modern applications compared to conventional capacitors or batteries [10].
Figure 1.8 shows several faradaic mechanisms proposed by Conway, which can result in pseudocapacitive behavior for capacitors [10, 15-19]. The first one is under potential deposition (UPD), which occurs when metal ions form an adsorbed monolayer at a different metal surface well above their redox potential. The deposition of lead on a gold surface is a representative example of UPD. The second type is the redox pseudocapacitance, this occurs during the process of the electrochemical adsorption of ions on the surface or absorption near the surface of material accompanied by a faradaic charge transfer. Transitional metal oxide, such as Fe₃O₄, NiFe₂O₄, RuO₂, Mn₃O₄, MnO₂, NiO, etc., as well as a conductive polymer, such as polyaniline and polypyrrole, are classified as the redox pseudocapacitive materials. The third one is the intercalation pseudocapacitance, which results from ion intercalation into the tunnels or layers of a redox-active material accompanied by a faradaic charge transfer but without crystallographic phase change [15].

![Diagrams of various redox mechanisms](image)

Figure 1.8 Various reversible redox mechanisms for pseudocapacitance [10].
1.3.3 Hybrid (asymmetric) supercapacitors

Typically, electric double-layer capacitors (EDLCs) and pseudocapacitors can be classified as symmetric supercapacitors as usually both positive and negative electrodes using the same type of material. However, to optimize the advantages of (EDLCs) and pseudocapacitors, recent researches tried to develop a combination between both types that released the newest category of the (ESs) named hybrid asymmetric supercapacitors [20]. The hybrid supercapacitors have relatively high specific energy as well as high specific power that fills the gap between the symmetric supercapacitors and Li-ion batteries. Figure 2.8 shows schematic structure and principles of hybrid asymmetric supercapacitor and illustrates electrostatic and electrochemical mechanisms of energy storage mechanisms [21].

Figure 1.9 Schematic structure and principles of a hybrid asymmetric supercapacitor [21].
The charge storage based on the pseudo mechanism is not limited to the surface only but also to the near-surface region where ions can diffuse into the active materials. The pseudo mechanism involves reversible redox reaction (Faradaic) during the charging or discharging process, in which the charges pass through the electrode/electrolyte interface; thus, the slow faradic process hindered the power performance. Conversely, EDLCs, which are based on electrostatic charge storage mechanism (non-Faradaic), whereas the charges just accumulate at the electrode/electrolyte interface in EDLCs [22].

The fabrication of efficient devices mainly depends on asymmetric hybrid supercapacitors, which optimize both high energy and power densities. This performance could be reached by a combination of two different electrode materials for both electrodes to fabricate a device. For instance, the transition metal oxide/carbon-based and conductive polymer/carbon-based material. Consequently, this structure enlarges the overall cell potential and results in higher energy density as well as power density [14, 22].

1.4 Active materials for supercapacitors applications

Many composites were developed to fill the gap in the performance between the battery and conventional capacitors. In other words, the development of different composite materials that could exhibit combined energy storage mechanisms (EDLC/Pseudo) [22]

1.4.1 Carbon-based materials

It was mentioned that EDLCs performance is controlled by the structure and surface area of active materials. For example, carbon-based materials have some advantages such as high surface area, good conductivity, high thermal stability, magnificent
corrosion resistance, and controllable porous structure that make them excellent candidates as active materials in EDLCs and as additives in pseudocapacitors [23]. Table 1 is a summary of different carbon materials and their related properties for EDLCs, such as carbon nanotube, graphene, activated carbon, and graphite [24-27].

Table 1.1 Carbon-based materials properties used in EDLCs.

<table>
<thead>
<tr>
<th>Material</th>
<th>Carbon onions</th>
<th>Carbon nanotubes</th>
<th>Graphene</th>
<th>Activated carbon</th>
<th>Carbidic derived carbon</th>
<th>Templated carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimensionality</td>
<td>0-D</td>
<td>1-D</td>
<td>2-D</td>
<td>3-D</td>
<td>3-D</td>
<td>3-D</td>
</tr>
<tr>
<td>Conductivity</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td>Moderate</td>
<td>Low</td>
</tr>
<tr>
<td>Volumetric capacitance</td>
<td>Low</td>
<td>Low</td>
<td>Moderate</td>
<td>High</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Cost</td>
<td>High</td>
<td>High</td>
<td>Moderate</td>
<td>Low</td>
<td>Moderate</td>
<td>High</td>
</tr>
<tr>
<td>Structure</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1.4.2 Redox-based materials

Compared to EDLCs, pseudocapacitors have a relatively higher capacity. Based on a redox reaction, the charges can accumulate both in an electrostatic way and in a faradaic reaction way [29, 30]

1.4.2.1 Conducting polymers

Conducting polymers have less pollution, easy fabrication and high conductivity, so they attract much attention in recent years. The popular conducting polymers are (i) polypyrrole (PPy), (ii) polyaniline (PAni), (iii) polythiophene (PTh), and (iv) poly(3,4-ethylene dioxythiophene) (PEDOT); Figure 1.10 shows their different molecular structures [31].
In the charge/discharge process, the charges are accumulated by the redox reaction-taking place in the bulk volume of the film, instead of just on the surface as the case in carbon. Therefore, the specific capacitance of (ESs) made by this kind of material is relatively high. However, there is a limitation of the conductive polymers that they can only be used within a rigid potential window [26].

1.4.2.2 Transition metal oxide materials

Table 1.2 below shows the common metal oxide materials for pseudocapacitors electrodes. It is obvious that RuO$_2$ has a high conductivity as well as a high capacitance. However, this kind of material is limited by its dangerous hazards and high cost. Thus, to replace RuO$_2$, inexpensive and non-toxic materials such as manganese oxide (MnO$_2$), vanadium oxide (V$_2$O$_5$), magnetite (Fe$_3$O$_4$), and nickel oxide (NiO) have been explored as pseudocapacitive materials. Among the metal oxides, Fe$_3$O$_4$ is chosen as the electrode material for supercapacitors due to its added merits such as high theoretical specific capacitance (2299 F g$^{-1}$), large potential window (-1.2 to 0.25 V), natural abundance, low cost, less toxicity, and ferrimagnetic properties [32, 33].
Table 1.2 Metal oxide materials for pseudocapacitors electrodes [14, 30 - 33].

<table>
<thead>
<tr>
<th>Metal oxide</th>
<th>Potential range (V)</th>
<th>Theoretical capacitance (F/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO₂</td>
<td>0.90</td>
<td>1380</td>
</tr>
<tr>
<td>NiO</td>
<td>0.50</td>
<td>2584</td>
</tr>
<tr>
<td>Co₃O₄</td>
<td>0.45</td>
<td>3560</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>1.00</td>
<td>2120</td>
</tr>
<tr>
<td>RuO₂</td>
<td>1.23</td>
<td>2200</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>1.45</td>
<td>2299</td>
</tr>
<tr>
<td>Mn₃O₄</td>
<td>1.10</td>
<td>1450</td>
</tr>
</tbody>
</table>

1.5 Mass loadings of electrodes

Despite the numerous attempts on the fabrication of advanced transition metal oxide composite electrodes, poor conductivity is one of the biggest challenges for metal oxide electrodes to become a practical application. It was demonstrated in the literature that Fe₃O₄ based composites thin-film electrodes could exhibit close to the theoretical capacitance of 215 F g⁻¹; however, the mass loading of the electrode was merely 4.3 mg cm⁻² [32]. It was pointed out that increasing mass loadings of electrodes drastically reduced the capacitances. He et al. have shown that by increasing the mass loading of MnO₂-graphene nanocomposites from 0.1 to 9.8 mg cm⁻², the capacitances decreased from 440 to 150 F g⁻¹ [32]. Higher mass loadings also reduce the performance of electrodes at higher scan rates due to poor electrolyte access. Another factor is the ratio of active materials mass to current collector mass (R). For thin-film electrode with 5 mg cm⁻² mass loading, the R ratio is 3.11x10⁻⁵ [33]. As the mass loadings increase, the R ratio becomes larger and more practical. However, there is a balance between a high R ratio and high capacitances.
Gogotsi et al. have suggested that a practical mass loading of electrodes should be above 10 mg cm$^{-2}$, such that the results are comparable on the Ragone plot [5]. Therefore, new current collectors and strategies must be employed to increase the $R_m$ ratio and preserve capacitive performance.

1.6 Dispersion of metal oxides

It was mentioned that high active surface area is an important factor in achieving high capacitance. However, in the colloidal fabrication of metal oxide nanoparticles, agglomeration of particles becomes one of the major challenges to utilize all surface areas. The driving force of agglomeration is the minimization of the surface energy of particles to be thermodynamically stable [34]. The drying procedure also promotes agglomeration due to the occurrence of condensation reactions between surface hydroxyl groups on the particles. When a solid particle emerges in solution, a surface charge will develop by either adsorption and desorption of ions or dissociation and substitution of surface charged species. Once the surface charge is developed, electrostatic repulsion will segregate positively and negatively charged species within the vicinity. Depending on the pH of the electrolyte, the surface of particles can be positively or negatively charged by adsorption of charge determining ions given by Eq.1.5 and Eq.1.6.

\[
M^{-}OH + H^{+} \leftrightarrow M^{-}OH_{2}^{+} \quad \text{(Eq. 1.5)}
\]

\[
M^{-}OH + OH^{-} \leftrightarrow M^{-}O^{-} + H_{2}O \quad \text{(Eq. 1.6)}
\]
Figure 1.11 shows the general surface charge vs the pH value and the isoelectric point (IEP), where the concentration of charge determining ions correspond to a charge-neutral surface and the IEP is different for various materials. At pH above the IEP, the reaction in Eq.1.6 dominates and yields a negatively charged surface, which is the case for the CCP synthesis of MNP Fe$_3$O$_4$ in DI water at pH 9. The surface charge developed by immersing particles in solutions can stabilize the suspension to a certain extent, and it is commonly referred to electrostatic stabilization [34].

![Figure 1.11 Schematic of surface charge of particles as a function of pH [34].](image)

In many cases, pure electrostatic repulsion is insufficient to provide good stabilization of colloids. Therefore, other stabilization techniques such as steric stabilization are employed. Steric stabilization typically uses polymers to act as a diffusion barrier for growth species, which can narrow the size distribution of particles as well as dispersion of colloids. There are three types of polymers based on their interactions with particles, anchored polymers, adsorbing polymers, and non-adsorbed polymers [34, 35].
Anchored polymers are polymers that interact with particles irreversibly by one end only; adsorbing polymers adsorb weakly on particles surface at random points of the polymers, and non-adsorbed polymers do not interact with particles surface and do not provide any steric stabilization. Anchored polymers are superior compared to adsorbing polymers, as adsorbing polymers can adsorb and bridge to other particles [36, 37]. Therefore, strong interactions with particles surface are an ideal property for the dispersant of particles. It has been demonstrated by Liu et al. that organic molecules with catechol group can provide strong adsorption to metal oxide particles for electrophoretic deposition (EPD). The investigation involved the analysis of carboxylic acids with different positions and amounts of hydroxyl groups on the aromatic ring. The acids that were investigated were caffeic acid (CA), trans-cinnamic acid (TCA), \( p \)-coumaric acid (PCA), and 2,4 di-hydroxycinnamic acid (DCA) and their chemical structure is shown in Figure 1.12. CA was the only acid that allowed the successful deposition of MnO\(_2\) particles using EPD [34, 35]. CA belongs to the catechol family, which contains an aromatic ring with two adjacent hydroxyl groups. Similar molecules can be found in protein macromolecules of mussels, containing catechol amino acid L-3-4dihydroxyphenylalanine (DOPA), adsorbing strongly to different substrates under wet conditions [35, 36].
Ata et al. have suggested a mechanism to describe superior adhesion of dispersants to metal oxide surface in which the strong adsorption to metal oxide particles was attributed to strong chelating and bridging mechanisms [37]. Figure 1.13 shows some multifunctional dispersing agents; some of them are positively charged molecules and others are positively charged. The positively charges ones such as 6-phosphonohexanoic acid (PHA) and pyrogallol red (PGR) could be used in the process of MnO$_2$ dispersion with advanced adsorption mechanism, and the negatively charged like azure A chloride (AZA) and Nile Blue chloride (NB) that could be used in dispersion with advanced adsorption mechanism for MWCNTs and Fe$_3$O$_4$ [37]. The presence of adjacent hydroxyl groups is crucial to strong bonding with metal oxide surface and for this reason, TCA, PCA, and DCA were unable to provide strong adhesion [35, 37].
1.7 Dispersion of MWCNTs

Carbon nanotubes (MWCNTs) tend to form bundles due to Van der Waals attractions and show poor solubility in aqueous and organic solvents [38,39]. There are several methods to disperse MWCNTs, and they typically involve covalent and non-covalent surface modifications. Covalent surface modifications involve surface functionalization by acid oxidation [40]. Aviles et al. have performed acid oxidation for MWCNTs using different oxidants and concentrations, such as \( \text{H}_2\text{SO}_4 \) and \( \text{HNO}_3 \). They have demonstrated that \( \text{HNO}_3 \) was able to oxidize the MWCNTs surface by introducing oxygen-containing functional groups on the surface [39]. The presence of functional groups led to a reduction of Van der Waals attractions between bundles and allowed separation and dispersion of MWCNTs. However, acid oxidation can reduce the length of MWCNTs and damage the surface continuity, which in turn degrade the mechanical and
electrical performance of MWCNTs [41]. Another approach to disperse MWCNTs is by non-covalent surface modifications, which avoid the performance degradation caused by surface functionalization [42]. Non-covalent surface modifications typically involve the use of polymers and head-tail surfactants as dispersing agents. The driving force of adsorption is the hydrophobic interactions of MWCNTs surfaces with long hydrocarbons chain in polymers and head-tail surfactants, and the hydrophilic groups give rise to dispersion [42]. However, it is difficult to avoid polymer wrapping of MWCNTs dispersed using polymers, resulted in an insulating polymeric layer on MWCNTs. Moreover, it was demonstrated that a large quantity of head-tail surfactants is required to achieve dispersion using sodium dodecyl sulfate (SDS) as a model of head-tail surfactant. Therefore, there is a need for efficient dispersants for MWCNTs, which do not compromise the structure and chemical integrity of MWCNTs [40-42].

1.8 Electrolytes for electrochemical supercapacitors (ESs)

One of the most valuable parameters in the ESs applications is the energy density enhanced electrolytes [43, 44]. The progress in the electrolytes could be considered as essential as the improvement of electrode materials because the potential window of electrolyte directly enhances the energy density [43]. In addition to the influence on energy density, the properties of electrolytes are contributed to the overall performance of ESs. Figure 1.14 illustrates the relation between different properties of electrolytes and some parameters that could judge the performance of ESs, such as capacitance, power density, etc. [43, 45].
Electrolytes could be classified into three main types; aqueous electrolytes, organic electrolytes, and ionic liquids-based electrolytes [43, 46]. Aqueous electrolytes and organic electrolytes are the most common electrolytes for ESs applications [43, 47].

1.8.1 Aqueous electrolytes

There are some advantages of the aqueous electrolytes compared to other types (organic – ionic) that make this type of electrolytes are widely used, such as the lower resistance, low cost, higher conductivity, and the high solubility of salts [43, 44, 48]. Normally, the resistivity of aqueous electrolytes is lower than that of organic electrolytes (for example, 1M H₂SO₄ has a conductivity of 0.8 S cm⁻² at 25 ℃), which is beneficial for the ESR [43, 44]. The main deficiencies of aqueous electrolytes are their small electrochemical stable potential window, which results in thermodynamic water decomposition at 1.229 V and low over potential, hydrogen evolution at the negative electrode with oxygen evolution at
positive electrode voltage that limits the window of aqueous electrolytes to around 1.2 V [43,48]. As shown in Figure 1.15, developments could extend the voltage window successfully was extended to 1.6 - 2.2 V by indicates that the asymmetric cell can be designed by choosing two different materials with different integrated potential voltage windows [43,46, 48].

The main divisions of aqueous electrolytes are neutral, acidic, and alkaline solutions. Electrolytes such as Na₂SO₄, NH₄Cl, H₂SO₄, KOH, and NaOH are mostly used in ESs applications due to high conductivity and ion transport mechanisms [48]. Neutral electrolytes are suitable for hybrid ESs with a wide voltage window. Furthermore, neutral electrolytes could be considered as a lower environmentally hazards assessment and low cost compared to acidic and alkaline. Among these electrolytes, Na₂SO₄ has been considered as the promising candidate for pseudocapacitors electrodes [44,47,48].

Figure 1.15 Potential windows of various electrode materials in aqueous electrolyte [48].
1.8.2 Organic electrolytes

The electrochemical performance of ESs that utilizes organic electrolytes is relying on the ion size, viscosity, conductivity, and electrochemical stability of the voltage window of the electrolyte [43]. In the presence of organic electrolytes, the ESs performance provides a relatively higher operation voltage window of about (2.2-2.8V) compared to aqueous electrolytes; therefore, the overall performance by exploiting the organic electrolytes shows enhanced energy density [43, 44]. However, ESs based on organic electrolytes obtained higher resistivity (20-60 Ω), low conductivity, and higher cost [43, 44, 47]. Propylene carbonate (PC) and triethylmethylammonium tetrafluoroborate (TEMABF$_4$) are the most commonly used solvents. PC-based electrolytes are considered lower in the environmental hazards and can contribute to the conductivity and the voltage window as well [43, 47].

1.8.3 Ionic liquid electrolytes

Ionic liquids (ILQs) are salts that exist as liquid at temperatures below 100°C and composed of a combination of organic cations and organic/inorganic anions. They are promising candidates for ESs because of their high thermal and chemical stability, non-flammable and non-corrosive properties, wide voltage window (~3.5–6 V), higher ionic conductivity relative to the organic electrolyte, and non-toxicity [49]. Ionic liquids (ILQs) promotes higher energy density because of the wider voltage range. Moreover, the high ionic concentration of (ILQs) has possibly reduced the electrolyte consuming problem, which significantly improved capacitor performance. Despite all these advantages, ILQs are too expensive for commercial applications and they are also hygroscopic that limits the handling of them and must be handled in the inert atmosphere [50].
Chapter 2

Problem statement and objectives

2.1 Gaps in the field of asymmetric hybrid supercapacitors

Based on the literature review, some gaps and problems have been found in the application of electrochemical supercapacitors that need more studies, especially the asymmetric hybrid type. We could summarize that, some of those problems are related to the structure of active materials and others to the design of the electrodes and devices.

2.1.1 Difficulties for dispersion of MWCNTs and agglomeration of MNPs

Carbon nanotubes (MWCNTs) have high relative conductivity and large surface area; however, their low specific capacitance limits their performance within the (ESs) [51]. On the other hand, MNPs such as NiFe$_2$O$_4$ and Fe$_3$O$_4$ could be considered as one of the most pseudocapacitive materials with high theoretical specific capacitance but poor electronic conductivity [51,52].

To optimize the advantages MNPs/MWCNTs composites in (ESs) application, NPs and MWCNTs particles should be as homogeneous as possible in addition to the reduction of the agglomeration of the particles [52,53]. Agglomeration of particles reduces the electrochemical performance by hinder the diffusion of ions into the electrodes. That agglomeration can be formed during the drying step of the composites, in addition to the presence of MWCNTs that always tend to aggregate easily [54,55]. Particle aggregation is governed by the reduction in particle surface area and condensation of the surface OH groups [54].
To address these problems, some attempts have demonstrated improvements and achieved high capacitances comparable to theoretical capacitances [33]. Several works have been focused on the covalent modification by generating acidic groups on the surface of MWCNTs to disperse them electrostatically and that’s through the oxidation of MWCNTs in strong acids [55]. Non Covalent functionalization methods are also utilized to disperse MWCNTs [56]. However, these strategies not only generate defects to MWCNTs but also reduces their mechanical properties, electronic conductivity and result in fractures [19, 20]. Therefore, new efficient processing techniques should be developed to fabricate electrodes with reduced agglomerated particles [56, 57].

![Figure 2.1 Schematic for surface modifications of MWCNTs [56].](image)

### 2.1.2 Low performance at high active mass loading

The success in the supercapacitor technology developments depends on the ability to utilize high specific capacitance of advanced materials with high active mass loadings [58]. The important task is to achieve good electrochemical performance at a high ratio of the active material mass to the current collector mass ($\delta_M$) [58, 59].
Metallic current collectors offer the benefits of high conductivity and low contact resistance [58-60]. However, the typical $\delta_M$ values for 1-5 mg cm$^{-2}$ films of active materials impregnated in metal foil current collectors lie below 0.01-0.02.

Figure 2.2 shows the CV profile for asymmetric device which shows the effect of increasing the active mass loadings [33]. Significantly, higher active mass loadings and ($\delta_M$) values are required for practical applications but without the limitation of decreasing the capacitance performance. The area normalized capacitance is another important parameter for the characterization of capacitor electrodes with high active mass loadings, especially for practical applications [8]. A high area normalized capacitance must be achieved with a low electrical resistance of the electrodes. Therefore, new current collectors and techniques should be developed to achieve high performance at high active mass loadings [33].

Figure 2.2 CV profile for asymmetric device shows the effect of increasing the active mass loadings [33].
2.1.3 Low capacitance of negative electrodes (unmatched capacitance)

In recent years, significant progress was achieved in the development of positive electrodes for supercapacitor devices [61]. However, the capacitance of negative electrodes is significantly lower compared to positive ones [62]. As a typical material for the positive electrode, MnO₂ provides a high specific theoretical capacitance of 1380 F g⁻¹ [63]. However, typical negative electrode materials such as activated carbon and Fe₂O₃ have very low capacitance for around 100 F g⁻¹ [64, 65]. As a result, the total device capacitance is limited by the low capacitance of negative electrodes as shown in (Figure 2.3) [62]. So advanced negative electrodes with new active materials such as magnetite (Fe₃O₄) that have high specific capacitance should be developed, magnetite has high theoretical specific capacitance (2299 F g⁻¹), a large potential window (-1.2 to 0.25 V), and a better cyclic stability in the range of negative electrodes [14, 65].

![CV profile for an asymmetric device](image)

Figure 2.3 CV profile for an asymmetric device shows the unmatched capacitance [62].
2.2 Objectives

Our objectives toward addressing the main problems in the (ESs) field are as follows:

➢ Long term:
  • Development of asymmetric hybrid supercapacitor electrodes and devices with enhanced performance at high active mass loading.

➢ Short term:
  • Development of advanced composites materials (Fe₃O₄ - MWCNTs) and (NiFe₂O₄ - MWCNTs) for supercapacitors' negative electrodes.
  • Development of advanced colloidal methods for the fabrication of composite materials for supercapacitors.
  • Development and testing of advanced asymmetric devices with large, stable voltage window.
Chapter 3
Methodology and experimental work

3.1 Synthesis of the M-CNTs by chemical co-precipitation (CCP) and liquid-liquid extraction method (PELLI)

Figure 3.1 shows the schematic diagram for the synthesis steps of Fe$_3$O$_4$-ACNTs (M-CNTs) composite materials using the liquid-liquid extraction method [62]. The adsorption depends on the electrostatic interaction and chemical heterocoagulation. Palmitic acid (PA) has been used as an extractor that depends on chemical heterocoagulation (chelation or bridging) through the specific chemical group (carboxylic group) with the metal ions of the M-CNTs that were precipitated from their salts by using the chemical co-precipitation (CCP).

Figure 3.1 Schematic for the fabrication of M-CNTs composite by liquid-liquid extraction methods.
3.2 Synthesis of the MNPs coated MWCNTs using multifunctional dispersants

Figure 3.2 shows the procedures of Synthesis of MNPs coated MWCNTs by using the CCP method and multifunctional dispersants. In the given schematic, M-CNTs with CB dye were presented in which Fe$^{2+}$, Fe$^{3+}$ salts, MWCNTs aqueous solutions, and ammonium hydroxide solutions have been used [37].

![Figure 3.2 Schematic for the fabrication of M-CNTs composites by using multifunctional dispersant.](image)

3.3 Material characterization

Several characterization techniques have been used to analyze the different parameters related to the materials synthesis and modifications processes as follow:
3.3.1 X-ray diffraction (XRD)

X-ray diffraction (XRD) analysis has been performed on the prepared sample, using the Bruker D8 DISCOVER instrument comprising DAVINCI diffractometer and Co-Kα radiation. The raw data were collected over a 2θ value then processed and analyzed using GADDS and EVA software by Bruker to generate a data file with intensity and corresponding 2θ value.

3.3.2 Transmission electron microscope (TEM)

Transmission electron microscope and scanning transmission electron microscope (STEM) were performed using a JEOL 2010F to study the morphology of the samples in addition to the elemental analysis that was done using STEM/EDX line and map scan.

3.3.3 RAMAN spectroscopy

Raman spectroscopy analyses were carried out using a laser wavelength of 514 nm (Renishaw BZ02- Spectra-Physics Lasers, USA). It was done for all synthesized, as purchased, and composite samples.

3.3.4 FTIR spectroscopy

FTIR measurements were carried out on a Bruker Vertex 70 spectrometer in the wavenumber range of 400 - 2000 cm\(^{-1}\).

3.4 Electrode fabrication by impregnation

The suspensions of active materials in ethanol solvent containing PVB were used for the impregnation of Ni foams.
3.5 Electrochemical characterization

Three main techniques of electrochemical analyzing that have been done are cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and Galvanostatic charge-discharge as follows:

3.5.1 Cyclic voltammetry

Cyclic voltammetry (CV) of single electrodes and for the device have been performed in 0.5 M Na$_2$SO$_4$ aqueous electrolyte using a potentiostat (PARSTAT 2273, Princeton Applied Research) shown in Figure 3.4 (A). Single electrodes were tested using three electrodes setup, where standard calomel electrode (SCE) was used as the reference electrode and platinum gauze as the counter electrode as shown in Figure 3.4(B), and the setup for the device is shown in Figure 3.4(C). The integral capacitances $C_S=Q/\Delta V S$ and $C_m= Q/\Delta V m$ were calculated using half the integrated area of the CV curve to obtain the charge Q and subsequently dividing the charge Q by the width of the potential window $\Delta V$ and electrode area S.
3.5.2 Electrochemical impedance spectroscopy

The electrochemical impedance spectroscopy (EIS) has been carried out using the PARSTAT 2273 potentiostat shown in Figure 3.4 (A). The alternating current measurements of complex impedance $Z^* = Z' - iZ''$ were performed in the frequency range of 10 mHz to 100 kHz at the amplitude of the signal of 5 mV. The complex differential capacitance $C_s^* = C_s' - iC_s''$ has been calculated from the impedance data as $C_s' = Z''/\omega|Z|2S$ and $C_s'' = Z'/\omega|Z|2S$, where $\omega = 2\pi f$ (f-frequency). The relaxation times $\tau = 1/fm$ were calculated from the frequency to correspond to the maxima of $C$ [7, 8].

3.5.3 Galvanostatic charge-discharge spectroscopy

Galvanostatic charge-discharge for single electrodes has been investigated in three-electrode cells by the analyzer (biologic VMP 300) shown in Figure 3.5 (A) using 0.5 M $\text{Na}_2\text{SO}_4$ aqueous electrolytes solutions. The counter electrode was a platinum gauze, and the reference electrode was a standard calomel electrode (SCE).
The charge-discharge behavior of the asymmetric device has been evaluated using the battery analyzers BST8-MA and BST8-3 (MTI Corporation, USA) shown in Figure 3.5 (B) at different current densities. Cyclic stability has been performed at a constant current density.

Figure 3.5 (A) Charge-discharge setup for single electrodes using analyzer (biologic VMB 300), (B) Battery analyzers (MTI Corporation, USA).
3.6 References


Chapter 4
High areal capacitance of Fe₃O₄-decorated carbon nanotubes for supercapacitor electrodes

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4.1 Abstract

A conceptually new approach has been developed for the fabrication of magnetite (Fe₃O₄)-decorated carbon nanotubes (M-CNTs) for negative electrodes of electrochemical supercapacitors. M-CNTs were prepared by an ultrasonic-assisted chemical synthesis method, which involved dispersion of functionalized CNTs in water, Fe₃O₄ formation on the CNTs surface, and particle extraction through liquid-liquid interface (PELLI). Palmitic acid was found to be an efficient new extractor for PELLI. The slurries produced after drying and re-dispersing M-CNTs and slurries obtained using PELLI were used for electrode fabrication. The electrodes prepared using PELLI showed superior performance due to reduced particle agglomeration. Testing results provided an insight into the influence of Fe₃O₄/CNTs mass ratio on the capacitance and capacitance retention at high charge-discharge rates. A capacitance of 5.82 F cm⁻² (145.4 F g⁻¹) was achieved in Na₂SO₄ electrolyte using electrodes with high active mass of 40 mg cm⁻² and ratio of active mass to current collector mass of 0.6. Good electrochemical performance was achieved at low impedance. The capacitance of the negative M-CNTs electrodes was comparable with capacitance of advanced positive MnO₂-CNTs electrodes, which was beneficial for the fabrication of asymmetric devices. The asymmetric device has been fabricated, which showed promising performance in a voltage window of 1.6 V.

Keywords: asymmetric device, capacitance, carbon nanotube, composite, magnetite, supercapacitor
4.2 Introduction

The surface modification of carbon nanotubes (CNTs) has received significant attention\(^1,\)\(^2\) due to many novel applications of CNTs that are decorated with various functional materials. The attractive properties of functionally decorated CNTs combine the high electrical and thermal conductivity of CNTs and their mechanical and optical properties with the functional properties of other materials. Various techniques have been developed to fabricate decorated CNTs, such as magnetron sputtering\(^3\), electrodeposition\(^4\), chemical precipitation\(^5\), atomic layer deposition\(^6\), pulsed laser ablation\(^7\), and chemical polymerization\(^8\).

Functionally decorated CNTs have integrated properties of CNTs and energy storage materials for battery applications and allowed for significant improvement in the capacity\(^3,\)\(^5\), cyclic stability\(^4\), and conductivity of batteries\(^9\). Multifunctional separators for batteries have been developed using CNTs decorated with TiO\(_2\) quantum dots\(^6\). It was found that CNTs, decorated with metals\(^10\), quantum dots\(^11\), and other photovoltaic materials\(^12\) enhanced the efficiency of solar cells. Of particular interest are applications of decorated CNTs as advanced catalysts for fuel cells\(^13\). In the field of supercapacitor devices for energy storage, investigations have been focused on the use of polypyrrole\(^14,\)\(^15\), activated carbon\(^16\), and oxide materials\(^17,\)\(^18\) for the decoration of CNTs. These studies have generated interest in the decorating CNTs with Fe\(_3\)O\(_4\) for use as electrodes of supercapacitors.
Fe₃O₄ is a promising pseudocapacitive material for negative electrodes of supercapacitors. The redox-active properties of Fe₃O₄ are related to Fe²⁺ and Fe³⁺ oxidation states. However, due to the low electronic conductivity of Fe₃O₄ and poor electrolyte access to the material surface, the specific capacitance decreases significantly with increasing active mass loading. Therefore, Fe₃O₄ is combined with conductive carbon additives to increase the overall electronic conductivity.

Fe₃O₄ electrodes containing different carbon materials, such as activated carbon, acetylene black, graphene, graphite, and CNTs have been developed and tested in different electrolytes, such as KOH, H₂SO₄, Na₂SO₃, and Na₂SO₄. Electrodes have been used with low active mass loadings in the 1 to 9 mg cm⁻² range. Fe₃O₄-decorated CNTs and Fe₃O₄-CNTs composite electrodes have shown promising capacitive properties. The enhanced performance of Fe₃O₄-based composite electrodes has been achieved in 1M H₂SO₄, 1M Na₂SO₃, and 6M KOH electrolytes. However, the use of Na₂SO₄ electrolyte offers benefits for fabricating asymmetric devices with a large voltage window and enhanced energy storage properties.

It has been found that Fe₃O₄-based negative electrodes, containing graphite and acetylene black, can complement a MnO₂-based positive electrode in a mild Na₂SO₄ electrolyte. The complementary potential windows of the individual electrodes allows for the formation of an aqueous device, operating in a voltage window of 1.8 V. A specific capacitance of 50 F g⁻¹ at a mass loading of 8.8 mg cm⁻² was determined for Fe₃O₄ negative electrode. The capacitance of the negative Fe₃O₄ electrode was significantly lower than that of positive MnO₂ electrode at the same electrode mass. In this case, larger mass of the
negative electrode was required to match total capacitance of the positive electrode. Therefore, further improvements in the technology of Fe₃O₄ electrodes are necessary to match the specific capacitance of MnO₂ electrodes and reduce the total mass of the device. Of particular importance is the development of advanced electrodes that have enhanced performance at mass loadings of about 10 to 20 mg cm⁻², which is required for practical applications.

The goal of this investigation was the fabrication of advanced Fe₃O₄-decorated CNTs for application in negative electrodes with high active mass loadings and high capacitance. A conceptually new approach has been developed for the magnetite-decorated carbon nanotubes (M-CNTs) fabrication. M-CNTs were prepared by an ultrasonic-assisted chemical synthesis method, which involved dispersion of functionalized CNTs in water, Fe₃O₄ formation on the CNTs surface, and application of particle extraction through liquid-liquid interface (PELLI) for the fabrication of well-dispersed particles. Palmitic acid (PA) was found to be an efficient new extractor for PELLI. The approach developed in this investigation allowed the fabrication of electrodes with an active mass of 40 mg cm⁻², which demonstrated a capacitance of 5.82 F cm⁻² (145.4 F g⁻¹). The areal capacitance obtained is significantly higher than the literature data for Fe₃O₄-based electrodes. Moreover, high capacitance was achieved at low impedance.

Analysis of experimental data provided insight into the influence of PELLI and mass ratio γ=Fe₃O₄/CNTs on capacitance and rate performance. The experimental results presented below indicate that the high capacitance of the Fe₃O₄-decorated CNTs negative electrodes practically matches the capacitance of MnO₂-CNTs positive electrodes in the Na₂SO₄
electrolyte at comparable active mass. The asymmetric capacitors, containing Fe₃O₄-decorated CNTs negative electrodes and MnO₂-CNTs positive electrodes showed promising performance.

4.3 Experimental procedures

Carbon nanotubes (CNT, Multiwalled, diameter 20-30 nm, length 1–2 µm, US Nanomaterial Inc, USA), FeCl₃·6H₂O, FeCl₂·4H₂O, NH₄OH, Palmitic acid (PA), polyvinyl butyral (PVB), Na₂SO₄, n-butanol (Sigma- Aldrich) and Ni foams (95 % porosity, Vale) were used. CNT were functionalized by treatment in concentrated nitric acid at 60 °C in ultrasonic bath for 4 hours. After washing, the acid treated CNT were dried in oven at 60 °C for 12 hours.

An ultrasonic-assisted chemical precipitation method has been used for the decoration of the activated CNTs with Fe₃O₄. In this method, acid-treated CNTs were dispersed in an aqueous solution of FeCl₂ and FeCl₃ (Fe²⁺:Fe³⁺ = 1:2) under ultrasonication and pH of the solution was adjusted to 9 using NH₄OH. The concentration of the iron salts was varied to obtain mass ratio γ = Fe₃O₄: CNTs in the range of 0.25 to 1.0. The obtained M-CNTs were used for the fabrication of electrodes.

The M-CNTs formed in an aqueous phase were filtrated. Obtained powders were washed, dried, and re-dispersed in ethanol. In another approach, M-CNTs were directly extracted to n-butanol by the PELLI method using PA as an extractor. The M-CNTs suspensions prepared by drying and re-dispersion or by PELLI method were used for impregnation of Ni foams. The PVB binder was added to the suspensions. The mass ratio PVB: M-CNTs was 0.03. The mass loading of 40 mg cm⁻² included the mass of M-CNTs.
and PVB binder. The obtained electrodes were used as anodes for asymmetric supercapacitor cells. The procedure for the fabrication of MnO₂-CNTs cathodes was described in a previous investigation 37.

Electron microscopy investigations were performed using Titan 80-300 LB transmission electron microscope (TEM). X-ray diffraction (XRD) studies were performed using a Bruker D8 diffractometer and Co Kα radiation. The electrochemical equipment for cyclic voltammetry, chronopotentiometry, and impedance spectroscopy testing of electrodes and devices were described in previous investigations 38,39. All the electrochemical testing experiments were performed using 0.5M Na₂SO₄ electrolyte.

4.4 Results and discussion

The formation of M-CNTs was confirmed by XRD, TEM and energy-dispersive X-ray spectroscopy (EDX) data. The comparison of the X-ray diffraction patterns (Figure 4.1) of Fe₃O₄ prepared without CNTs, M-CNTs and CNTs showed that M-CNTs contained peaks of both: Fe₃O₄ and CNTs.
Figure 4.1 X-ray diffraction patterns of (a) Fe₃O₄ powder, (b) M-CNTs, and (c) acid-treated CNTs. ▼, JCPDS file 19 - 0629; ●, JCPDS No. 41 - 1487; M-CNTs, magnetite - decorated carbon nanotube.

Figure 4.2 (A) shows scanning transmission electron microscope of M-CNTs. The image indicates that CNTs were decorated with nanoparticles. The typical size of the nanoparticles was below 25 nm. The EDX scan Figure 4.2 (B) confirmed that the particles contained Fe. It is known that nitric acid treated CNTs contain carboxylic groups, which facilitate CNTs dispersion. We suggested that such carboxylic groups promoted Fe₃O₄ nanoparticle synthesis on the CNTs surface. The M-CNTs were used for the fabrication of negative electrodes of supercapacitors.
Figure 4.2  A, STEM image; B, EDX line scan for Fe (the line is shown in (A)). EDX, energy-dispersive X-ray spectroscopy; STEM, scanning transmission electron microscope.

The use of commercial Ni foam current collectors was critical for the fabrication of electrodes with high active mass loading. However, the formation of suspensions for the impregnation of Ni foam current collectors presented difficulties due to M-CNTs agglomeration that resulted from the Van der Waals and magnetic attraction forces. The high aspect ratio of M-CNTs is another factor promoting agglomeration and sedimentation. Therefore, PELLI method has been developed to reduce M-CNTs agglomeration. This method requires careful selection of an extractor, which must be soluble in an organic solvent and adsorbed on particles at the liquid-liquid interface.
The extraction efficiency was close to 100%. Figure 4.3 (A) shows a chemical structure of PA that was used as an extractor for PELLI. PA is a typical head-tail surfactant, containing a hydrophobic hydrocarbon group, which facilitated PA dissolution in n-butanol. The carboxylic group of PA allowed for PA adsorption on Fe$_3$O$_4$ by chelating or bridging bonding Figure 4.3 (B). Similar to other surfactants, PA accumulated at the liquid-liquid interface with the hydrophilic carboxylic groups exposed to the aqueous phase. The extraction mechanism involved PA adsorption on the particles at the liquid-liquid interface and particles transfer to the n-butanol phase.

Figure 4.3 A, Chemical structure of PA; B, adsorption mechanisms, involving Fe atoms on the particle surface and carboxylic acid group of PA: (a) chelation, (b) bridging. PA, Palmitic acid.

Testing of the electrodes revealed benefits of extracted M-CNTs, as compared to dried and re-dispersed M-CNTs. Figure 4.4 compares cyclic voltammetry dependences (CVs) for electrodes with $\gamma = 0.40$ and $\gamma = 1.00$. The M-CNTs electrodes prepared using PELLI showed significantly larger CVs areas, compared with M-CNTs formed by a traditional drying and re-dispersion method at the same scan rates.
Figure 4.4 CVs at scan rates of (a) 2, (b) 5, and (c) 10 mV s\(^{-1}\) for M-CNTs electrodes, prepared (A, B) without PELLI and (C, D) using PELLI for (A, C) \(\gamma = 0.40\) and (B, D) \(\gamma = 1.0\). M-CNTs, magnetite-decorated carbon nanotube; PELLI, particle extraction through liquid-liquid interface.

The capacitances of the electrodes with different \(\gamma\) were calculated from CV data at different scan rates and presented in (Figure 4.5). The M-CNTs electrodes prepared using PELLI showed higher capacitances. The benefits of PELLI are especially evident for \(\gamma = 0.7\) and \(\gamma = 1.0\). The highest capacitance of 5.82 F cm\(^{-2}\) (145.4 F g\(^{-1}\)) was obtained at a scan rate of 2 mV s\(^{-1}\) for M-CNTs electrodes with \(\gamma = 1.00\). Such electrodes showed a capacitance retention of 37% at a scan rate of 100 mV s\(^{-1}\). The capacitance of the M-CNTs electrodes
prepared using PELLI for $\gamma = 1.00$ was significantly higher, compared with literature data for the capacitance of other Fe$_3$O$_4$-based electrodes, which were described in Section 1.

Figure 4.5  $C_s$ and $C_m$ vs scan rate for M-CNTs: A, prepared without PELLI and B, using PELLI for (a) $\gamma = 1.0$, (b) $\gamma = 0.70$, (c) $\gamma = 0.55$, (d) $\gamma = 0.40$, and (e) $\gamma = 0.25$. M-CNTs, magnetite-decorated carbon nanotube; PELLI, particle extraction through liquid-liquid interface.

The M-CNTs electrodes with $\gamma = 0.55$ and $\gamma = 0.7$ prepared using PELLI showed capacitances of 3.88 $F cm^{-2}$ (97.1 $F g^{-1}$) and 2.12 $F cm^{-2}$ (53.1 $F g^{-1}$) at 2$mV s^{-1}$, and capacitance retentions of 51% and 65%, respectively. The increase in capacitance with increasing $\gamma$ resulted from the higher capacitance of Fe$_3$O$_4$, as compared with that of CNTs. However, better capacitance retention was obtained at lower $\gamma$ values. The capacitance of electrodes usually decreases with increasing scan rate, especially for high active mass. Such decrease is related to diffusion limitations of electrolyte in pores of electrode material. The impregnation of electrodes without PELLI presented difficulties. In this case, the material was accumulated close to the current collector surface and blocked electrolyte access. As a result, the capacitance was low, but it was less influenced by the scan rate.
Using PELLI we enhanced capacitance significantly, especially for low scan rates and $\gamma = 1$. However, the diffusion limitations resulted in capacitance reduction with increasing scan rate and lower rate performance.

The analysis of the impedance data provides additional evidence of the beneficial effect of the decorated CNTs and the PELLI method. The M-CNTs electrodes exhibited a relatively low real part of the impedance due to good contact of Fe$_3$O$_4$ and CNTs in the decorated CNTs (Figure 4.6). The electrodes prepared using PELLI showed a lower real part of the impedance, as compared with the electrodes, prepared without PELLI. The differential capacitances $C_s'$, calculated from the impedance data at different frequencies were higher for the electrodes prepared using PELLI. The analysis of differential capacitances at different frequencies revealed relaxation type dispersions (Figure 4.6). The use of PELLI resulted in lower charge transfer resistance due to better impregnation of the current collectors with active material. Moreover, the electrodes prepared using PELLI showed slight increase in the relaxation frequency, as compared with the electrodes, prepared without PELLI.
Figure 4.6 EIS data for M-CNTs electrodes, prepared (A, B, C) without PELLI and (D, E, F) using PELLI: (A, D) Nyquist plot of complex impedance and frequency dependences of (B, E) $C_s'$ and (C, F) $C_s''$ for (a) $\gamma = 0.40$, and (b) $\gamma = 1.00$. EIS, electrochemical impedance spectroscopy; M-CNTs, magnetite-decorated carbon nanotube; PELLI, particle extraction through liquid-liquid interface.

The chronopotentiometry data showed nearly ideal symmetrical triangular shapes of the charge-discharge curves at different current densities Figure 4.7 (A). The capacitances of the electrodes were also calculated from the constant current discharge data and presented in Figure 4.7 (B). The capacitance of 5.2 F cm$^{-2}$ was obtained at a discharge current of 3mA cm$^{-2}$ for electrode, prepared using PELLI. The capacitance decreased with increasing current density to the level of 4.2 F cm$^{-2}$ at 20 mA cm$^{-2}$. The electrode, prepared without PELLI showed significantly lower capacitance Figure 4.7 (B).
Testing results indicated that the capacitance of the electrodes depended on different parameters, such as scan rate, current density, alternating current (AC) frequency, and voltage. The comparison of the data at similar charge-discharge time revealed lower AC differential capacitance, compared with the integral capacitances, derived from the CV and chronopotentiometry data. The difference can be attributed to reduced electrolyte access to the active material at low AC voltage.

The relatively high capacitance of the electrodes prepared using PELLI is promising for the fabrication of asymmetric devices with enlarged voltage window in Na$_2$SO$_4$ electrolyte. The use of Na$_2$SO$_4$ electrolyte offers advantages, compared with Na$_2$SO$_3$.

It is known that advanced materials for positive electrodes, such as MnO$_2$, exhibit excellent capacitive performance in Na$_2$SO$_4$. Moreover, asymmetric capacitor cells with
enlarged voltage window can be fabricated using this electrolyte. Turning again to the literature data [34] on the fabrication of Fe$_3$O$_4$/MnO$_2$ asymmetric devices, it is seen that the active mass ratio of MnO$_2$/Fe$_3$O$_4$ (R) was R = 0.33. The larger mass of Fe$_3$O$_4$ electrode$^{34}$ was necessary to match the capacitance of the positive electrode. The approach developed in our investigation allowed for significantly higher specific capacitance (145.4 F g$^{-1}$) of the M-CNTs electrodes, as compared with the specific capacitance of Fe$_3$O$_4$ composites (50 F g$^{-1}$), reported in the literature$^{34}$. The higher capacitance was achieved at significantly higher active mass. The high areal capacitance of 5.82 F cm$^{-2}$ obtained at 2mV s$^{-1}$ for negative M-CNTs electrodes ($\gamma=1$) at active mass of 40 mg cm$^{-2}$ was close to the capacitance of 5.81 F cm$^{-2}$ at 2mV s$^{-1}$ for MnO$_2$-CNTs electrode achieved $^{37}$ at an active mass of 35 mg cm$^{-2}$. Therefore, good capacitance matching can be achieved at 2 mV s$^{-1}$ for mass ratio of negative/positive electrodes R = 0.88. However, MnO$_2$-CNTs electrodes showed $^{37}$ better capacitance retention at scan rates in the range of 2 to 20 mV s$^{-1}$. Therefore, the mass of the negative electrode was increased to match the capacitance of the positive electrode at a scan rate of 20 mV s$^{-1}$. The desired ratio of R = 0.7 was obtained using 10 × 10 mm positive electrodes and 11 × 11 mm negative electrodes. The obtained asymmetric device showed good capacitive behavior in a voltage window of 1.6 V, as indicated by nearly box shape CVs Figure 4.8 (A).

The average electrode area was used for the calculation of areal capacitance for the device at different scan rates Figure 4.8 (B). The areal capacitance of 2.3 F cm$^{-2}$ was obtained at a scan rate of 2mV s$^{-1}$. EIS data showed that real part of the impedance increased, compared with that for the individual components Figure 4.8 (C).
The total electrode resistance included the resistance of the individual electrodes and electrolyte in pores of a separator membrane. The relaxation frequency of the device shifted to lower frequencies, as compared with the relaxation frequencies of the individual electrodes Figure 4.8 (D, E).

Figure 4.8  A, CVs at scan rates of (a) 2, (b) 5, and (c) 10 mV s\(^{-1}\); B, \(C_S\) and \(C_m\) vs scan rate; C, Nyquist plot of complex impedance and frequency dependences of D, \(C_S'\) and E \(C_S''\) for an asymmetric supercapacitor cell, containing MnO\(_2\)-CNTs as a positive electrode and M-CNTs (\(\gamma = 1.0\)). Prepared using PELLI as a negative electrode. M-CNTs, magnetite-decorated carbon nanotube; PELLI, particle extraction through liquid-liquid interface.
The chronopotentiometry studies showed symmetrical triangular charge-discharge curves at various current densities Figure 4.9 (A). A capacitance of 2.7 F cm\(^{-2}\) was obtained at a discharge current density of 3 mA cm\(^{-2}\). The capacitance decreased with increasing current density Figure 4.9 (B), the capacitance retention at 50mA cm\(^{-2}\) was 75%. The chronopotentiometry data was used to calculate the power density and energy density at different current densities.

Figure 4.9  A, Charge‐discharge curves at current densities of (a) 3, (b) 5, (c) 10, (d) 20, (e) 30, (f) 40, and (g) 50 mA cm\(^{-2}\); B, \(C_s\) and \(C_m\) vs. current density for an asymmetric supercapacitor cell, containing MnO\(_2\)-CNTs as a positive electrode and M-CNTs (\(\gamma = 1.0\)) prepared using PELLI as a negative electrode. M-CNTs, magnetite-decorated carbon nanotube; PELLI, particle extraction through liquid-liquid interface.

The data are presented in a Ragone plot (Figure 4.10 (A)), which indicate that relatively high power-energy characteristics were obtained for the asymmetric device with high active mass. High power energy characteristics have also been reported in other investigations \(^{42-44}\). It is important to note that specific capacitance, power density, and energy density
decrease significantly with increasing active mass. Therefore, good electrochemical performance at high active mass, achieved in our investigation, is promising for practical applications. Of particular importance is that in this investigation a high capacitance was achieved at low impedance. Another important factor is mass ratio of active mass to current collector mass ($\delta_M$). In our investigation good electrochemical performance of M-CNTs electrodes was achieved at a relatively high $\delta_M = 0.6$. The device showed a capacitance retention of 87% after 3000 cycles and Coulombic efficiency of 100% Figure 4.10 (B).

Figure 4.10 A, Ragone plot for an asymmetric supercapacitor cell, containing MnO$_2$-CNTs as a positive electrode and M-CNTs ($\gamma = 1.0$) prepared using PELLI as a negative electrode; B, (a) capacitance retention and (b) Coulombic efficiency vs cycle number. M-CNTs, magnetite-decorated carbon nanotube; PELLI, particle extraction through liquid-liquid interface.
4.5 Conclusions

Fe₃O₄-decorated CNTs were prepared by an ultra-sonic assisted chemical synthesis method, which involved the dispersion of functionalized CNTs in water and Fe₃O₄ nanoparticle formation on the CNTs surface. The use of PA as an extractor for PELLI facilitated the transfer of M-CNTs from an aqueous synthesis medium to an organic medium for electrode fabrication. PELLI allowed for reduced M-CNTs agglomeration and improved impregnation of Ni foam current collectors. The M-CNTs electrodes, prepared using PELLI, showed higher capacitance and lower resistance, as compared with M-CNTs electrodes prepared without PELLI. Good electrochemical performance was achieved at a high active mass loading of 40 mg cm⁻².

The highest capacitance of 5.82 F cm⁻² (145.4 F g⁻¹) was achieved for γ=1 at 2mV s⁻¹, however the electrodes with lower γ showed better capacitance retention at high scan rates. Enhanced electrochemical performance of M-CNTs electrodes was achieved at a low impedance and relatively high δM = 0.6. The capacitance of the negative M-CNTs electrodes prepared using PELLI was comparable with capacitance of advanced positive MnO₂-CNTs electrodes, which was beneficial for the fabrication of asymmetric devices. The asymmetric device has been fabricated, which showed promising performance in a voltage window of 1.6 V.

4.6 Acknowledgement

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4.7 References


4.8 Supporting informations

Figure 4.11 (A) PELLI for M-CNTs by PA (B) Separation of the inorganic phase with the impurities and sideproducts.
Chapter 5

Fe$_3$O$_4$ spinel-Mn$_3$O$_4$ spinel supercapacitor prepared using Celestine blue as a dispersant, capping agent and charge transfer mediator

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5.1 Abstract

An asymmetric spinel-spinel supercapacitor is fabricated with negative and positive electrodes consisting of Fe₃O₄ and Mn₃O₄ nanoparticles, respectively, where carbon nanotubes (CNT) serve as conductive additives. High performance of the individual electrodes and devices is achieved at a high active mass (AM) loading of 40 mg cm⁻² for the individual electrodes. A conceptually new strategy is based on the use of multifunctional Celestine blue (CB) dye, which is strongly adsorbed on the spinel phases and CNT, facilitates dispersion, acts as a capping agent and allows for the fabrication of spinel decorated CNT. Moreover, it is discovered that CB is an efficient charge transfer mediator, which allows for significant improvement of capacitive behavior. The use of CB as a charge transfer mediator allows for good utilization of capacitive properties of spinels at high AM. Mechanisms of spinel-CB-CNT interactions and charge transfer mediation are discussed. The capacitive properties are analyzed by cyclic voltammetry, chronopotentiometry and impedance spectroscopy for the electrodes with different spinel/CNT mass ratios. The areal capacitances of 6.17 and 5.15 F cm⁻² are obtained for Fe₃O₄ and Mn₃O₄ based electrodes, respectively in 0.5 M Na₂SO₄ electrolyte. The high capacitances are achieved with low electrode resistance. The electrodes are used for the fabrication of an asymmetric device which shows a capacitance of 2.41 F cm⁻² in a voltage window of 1.6 V.

Key words: spinel, iron oxide, manganese oxide, carbon nanotube, supercapacitor, charge transfer, dispersant, composite
5.2 Introduction

Due to their multiple valence states, high capacitance, low cost, and chemical stability, transition metal oxides are used to fabricate electrodes for electrochemical supercapacitors. Interest has been focused on individual oxides, such as MnO$_2$, Mn$_3$O$_4$, Fe$_2$O$_3$, Fe$_3$O$_4$, Co$_3$O$_4$, NiO [1-6] and complex oxides [7-9]. There are excellent reviews, which describe advanced materials, charging mechanisms, electrode design and performance of metal oxide based supercapacitors [3, 4, 7, 10].

A major problem in the development of metal oxide supercapacitor technology is poor electrode performance at commercially desirable high active mass (AM) loadings [11]. Many metal oxide materials showed outstanding capacitive properties, such as high gravimetric capacitance (F g$^{-1}$) and low impedance, only for AM lower than 1 mg cm$^{-2}$. However, the total capacitance of such electrodes is low. Moreover, the electrodes show very low ratio of active material mass to the mass of current collector (Rm). Thin films with active mass < 1 mg cm$^{-2}$ on metal foil substrates have R$_m$ < 0.01[12]. The devices with low AM have low total capacitance and high total mass, which includes mass of active materials, electrolyte, current collectors and other passive components. The AM loading for practical applications must be above 10–20 mg cm$^{-2}$ [13-15]. However, it is challenging to achieve good electrochemical performance at high AM.

A significant decrease in specific capacitance with increasing capacitive material AM results from the poor electronic and ionic conductivities [11] of metal oxide based electrodes. Therefore, advanced technologies must be developed for the synthesis of
nanoparticles and their mixing with conductive additives on the nanometer scale. The modification of chemical composition is another important avenue for the development of advanced materials. It is important to note that tremendous progress in the development of advanced ceramic materials in different fields has been achieved by the synthesis of solid solutions, which exhibited superior properties. Advanced spinel solid solutions have been developed for magnetic applications [16, 17], batteries [18, 19], photoelectrochemical, and photocatalytic applications [20, 21].

Spinel-type oxide materials are of interest for supercapacitors [9, 22]. Such materials can be prepared by chemical precipitation at room temperature [22, 23]. Spinel solid solutions can be synthesized at room temperature or at relatively low temperatures under hydrothermal conditions [24]. The ability to form individual spinel compounds and solid solutions by chemical precipitation allows the fabrication of nanoparticles of controlled size. The synthesis of Mn₃O₄ spinel offers very promising processing advantages for the fabrication of positive electrodes of supercapacitors. For comparison, MnO₂ is another very promising cathode material, which is usually prepared by the reduction of Mn⁷⁺ in permanganate solutions. However, permanganates react with organic capping agents and conductive carbon additives. Such reactions result in decomposition of the capping agents and conductive additives. Therefore, organic capping agents cannot be used for the modification of particle size and morphology during synthesis. As a result, there has been limited progress in the fabricating MnO₂ nanoparticles of small size for design of advanced nanocomposite. The decomposition of carbon additives in chemical reactions with permanganates results in their oxidation and conversion to CO₂ gas. Therefore, conductive
additives cannot be added during synthesis. This limitation is detrimental for the formation of advanced nanocomposite with improved mixing of the individual components. In contrast, Mn$_3$O$_4$ can be produced from Mn$^{2+}$ solutions in the presence of capping agents, which limit particle growth. Moreover, the use of Mn$^{2+}$ precursors paves the way for the fabrication of advanced composites using new techniques for synthesis, co-dispersion and enhanced mixing of the individual components. Recent studies [23] showed that capacitance of Mn$_3$O$_4$-CNT cathodes, prepared using capping agents and advanced colloidal techniques, was higher than the capacitance of MnO$_2$-CNT cathodes at AM loading of 33 mg cm$^{-2}$. Mn$_3$O$_4$ forms spinel solid solutions, which are promising for the modification of electrode properties.

Fe$_3$O$_4$ is another promising spinel material for negative electrodes. Asymmetric devices, containing Fe$_3$O$_4$ as a negative electrode and MnO$_2$ as a positive electrode have an enlarged voltage window of 1.8 V in aqueous K$_2$SO$_4$ electrolyte. A capacitance of 50 F g$^{-1}$ has been reported at mass loading of 8.8 mg cm$^{-2}$ for composite Fe$_3$O$_4$-based electrodes [25]. However, the gravimetric capacitance of the negative electrodes was significantly lower than that of the positive electrodes. Matching the total capacitances of the individual electrodes generates a need in significantly larger AM of the negative electrode, compared to the AM of the positive electrode. Therefore, the specific capacitance of the negative electrodes must be increased. Moreover, good performance must be achieved at high AM.

The objective of this investigation was to fabricate spinel-spinel asymmetric supercapacitor devices using spinel Fe$_3$O$_4$ and Mn$_3$O$_4$ materials for anodes and cathodes, respectively. Our new approach is based on the application of Celestine blue (CB) as a
multifunctional capping dispersant for the synthesis of spinel phases in the presence of dispersed CNT, which were used as conductive additives. This approach resulted in the formation of spinel nanoparticle decorated CNT. Celestine blue (CB) was used as a charge transfer mediator, which allowed for significant capacitance enhancement. Good nanotube dispersion was achieved using CB as an efficient aromatic dispersant, offering the advantages of good adsorption on CNT, small size and ability to disperse CNT at low CB dispersant concentrations. The positive charge and chelating properties of CB promoted spinel phase formation on the surface of CNT due to chemical bonding and electrostatic heterocoagulation mechanisms.

Moreover, CB acted as a capping agent, which allowed for the particle size reduction. Good performance of the electrodes was achieved at AM of 40 mg cm\(^{-2}\). We achieved exceptionally high capacitance of the negative electrodes, which facilitated the development of advanced asymmetric devices.

5.3 Experimental procedures

Iron (II) chloride tetrahydrate (FeCl\(_2\)·4H\(_2\)O), iron (III) chloride hexahydrate (FeCl\(_3\)·6H\(_2\)O), manganese nitrate tetrahydrate (Mn (NO\(_3\))\(_2\) ·4H\(_2\)O), ammonium hydroxide (NH\(_4\)OH), sodium hydroxide (NaOH), sodium sulfate (Na\(_2\)SO\(_4\)), Celestine blue (CB) and polyvinyl butyral (PVB, average MW = 50–80 kDa) were purchased from Sigma Aldrich. Multiwalled carbon nanotubes (CNT, purity > 95%, OD 20–30 nm, and length 1–2 μm) were purchased from US Nanomaterial Inc, USA. Vale Ltd., Canada, supplied Ni foam (porosity of 95%).
Nanoparticles of $\text{Fe}_3\text{O}_4$ were prepared by chemical precipitation. The stoichiometric amounts of $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ salts were dissolved in DI water, and the pH of the solution was adjusted to $\text{pH} = 9$ by adding $\text{NH}_4\text{OH}$. The reaction was carried out at $70\, ^\circ\text{C}$ with a supply of $\text{N}_2$ gas. The mixed $\text{Fe}_3\text{O}_4$ and CNT sample was prepared by dispersing $1\, \text{g L}^{-1}$ of CNT in DI water and ultrasonicating for 45 min. Subsequently, $0.25\, \text{g L}^{-1}$ of CB was added to the CNT suspension, which was then ultrasonicated for 15 min, $1\, \text{g L}^{-1}$ $\text{Fe}_3\text{O}_4$ in aqueous solution was then mixed with $1\, \text{g L}^{-1}$ CNT suspension, containing CB, and ultrasonicated for 60 min. The dispersion was filtrated, washed, and dried overnight in an oven at $60\, ^\circ\text{C}$. A similar procedure was carried without CB to analyze the influence of CB on the electrode performance.

For the in-situ synthesis of $\text{Fe}_3\text{O}_4$ in the presence of CNT and CB, a $1\, \text{g L}^{-1}$ CNT suspension, containing $0.25\, \text{g L}^{-1}$ CB was initially prepared. Stoichiometric amounts of $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ salts were dissolved in DI water, and added to the CNT suspensions to obtain oxide/CNT mass ratio $\gamma$ of 1, 1.25, 1.5, and 2.0. The synthesis procedure was similar to that for pure $\text{Fe}_3\text{O}_4$, as it was described above. Table 5.1 (Supporting information) presents data on the composition of the tested samples and methods of their preparation. The synthesis of $\text{Mn}_3\text{O}_4$ nanoparticles has been previously described [26]. Similar to $\text{Fe}_3\text{O}_4$-CNT composites, the $\text{Mn}_3\text{O}_4$-CNT composites with different $\gamma$ were also prepared by in-situ synthesis of $\text{Mn}_3\text{O}_4$ in the presence of CNT, that were dispersed using CB. To fabricate the electrodes, the dried $\text{Fe}_3\text{O}_4$-CNT and $\text{Mn}_3\text{O}_4$-CNT composites were dispersed in ethanol containing 3% PVB. The obtained slurry was used to impregnate Ni foam current collectors. The active mass loading of the electrodes was $40\, \text{mg cm}^{-2}$. 
Transmission electron microscopy was performed using a JEOL 2010F field emission microscope. The elemental analysis was done using energy dispersive X-ray spectroscopy (EDX). X-ray diffraction (XRD) analysis was performed using the Bruker D8 DISCOVER instrument comprising DAVINCI diffractometer and Co-Kα radiation. Raman spectroscopy analysis was carried out using Renishaw InVia Raman Spectrometer and a laser excitation wavelength of 514 nm (Spectra Physics Lasers, USA).

Cyclic voltammetry (CV) and alternating current (AC) electrochemical impedance spectroscopy (EIS) of the single electrodes and asymmetric devices were performed as described in prior investigations [12, 27]. Galvanostatic charge–discharge was performed using Biologic VMP 300 potentiostat at current densities of 3, 5, 7, and 10 mA cm⁻². The charge-discharge behavior of the asymmetric devices, containing Mn₃O₄-CNT positive electrodes and Fe₃O₄-CNT negative electrodes was evaluated using battery analyzers BST8-MA and BST8-3 (MTI Corporation, USA) at current densities of 3–50 mA cm⁻². Areal capacitance Cs (F cm⁻²) and mass normalized capacitance Cm (F g⁻¹) were calculated from the CV and galvanostatic charge-discharge data as described in prior investigations [12, 27]. Complex AC capacitance \( C^* = C' - iC'' \) was calculated from the impedance data [12, 27].

5.4 Results and discussion

Fe₃O₄ is a promising charge-storage material for supercapacitor anodes. However, it is challenging to achieve good performance of this material at high AM. The development of advanced anodes with high AM requires the fabrication of non-agglomerated Fe₃O₄ particles, which must be well mixed with dispersed CNT. Charge transfer between Fe₃O₄
and conductive additives is one of the challenges in the design of electrodes with high AM.

Metal oxide nanoparticles and CNT are prone to agglomeration due to their high surface area. In aqueous processing techniques, the surface condensation reactions of OH⁻ groups promote the formation of hard agglomerates of metal oxide nanoparticles. In the case of ferrimagnetic Fe₃O₄, particle agglomeration is further enhanced through inter-particle magnetic attraction. These challenges were addressed by the development of Fe₃O₄-decorated CNT using CB mediated in-situ synthesis. We report multiple findings that demonstrate the benefits of CB for fabricating advanced electrodes with enhanced performance at high AM.

Figure 5.1 (A) shows the chemical structure of CB. The polyaromatic structure of CB is beneficial for its adsorption on CNT. The CB adsorption mechanism is based on the formation of π-bonds. The small size of the CB molecule and its strong adsorption on CNT facilitated the CNT dispersion Figure 5.1 (B) by unzipping mechanism [28]. The interaction of CB with Fe₃O₄ particles can involve two possible mechanisms Figure 5.1(C). One mechanism is based on the chelating catechol-type CB bonding to the Fe atoms on the surface of Fe₃O₄ particles Figure 5.1 (C). Recent studies highlighted unique benefits of this bonding mechanism, which was used for the development of advanced chelating dispersants [29]. The interest in the catechol-type bonding resulted from the investigations of strong mussel's proteins adsorption on inorganic surfaces. Another mechanism involves the electrostatic interactions. The synthesis of Fe₃O₄ was performed at pH = 9-10 which is higher than the isoelectric point (pH = 6.5) [30] of this material. As a result, the synthesized particles were negatively charged and attracted cationic to CB.
In this investigation, we dispersed CNT using CB and then performed in-situ synthesis of \( \text{Fe}_3\text{O}_4 \) in the presence of dispersed CNT. The CB-CNT and CB-\( \text{Fe}_3\text{O}_4 \) interactions led to the formation of \( \text{Fe}_3\text{O}_4 \)-decorated CNT (FDCNT), as it is shown schematically in Figure 5.1 (D).

The formation of FDCNT allowed for improved contact of capacitive \( \text{Fe}_3\text{O}_4 \) and conductive CNT. Moreover, it will be shown below that catechol- type bonding of CB to \( \text{Fe}_3\text{O}_4 \) particles Figure 5.1 (C) and redox properties of CB, described by a reaction presented in Figure 5.1(E), facilitated charge transfer.
Figure 5.1  (A) chemical structure of cationic CB, containing a chelating catechol group, (B) unzipping mechanism of CNT dispersion using CB, (C) interaction of CB with Fe$_3$O$_4$ particles: chelating bonding and electrostatic attraction, (D) schematic of Fe$_3$O$_4$ decorated CNT and CB interaction with both materials, (E) redox reaction of CB.

Figure 5.2 compares the XRD pattern of a mixture of CNT and Fe$_3$O$_4$, prepared by a chemical precipitation method, with a diffraction pattern of FDCNT. The diffraction patterns show peaks corresponding to Fe$_3$O$_4$ (JCPDS file 19–0629) and CNT (JCPDS file 22–1012) for both samples.
The broadening of the Fe$_3$O$_4$ diffraction peaks for FDCNT is attributed to low crystallite size. The observed broadening could be attributed to the effect of CB, which acted as a capping agent. The peak broadening resulted in reduced relative intensity of the Fe$_3$O$_4$ peaks. Changes in the relative intensity of the FDCNT peaks, compared to the mixture of CNT and Fe$_3$O$_4$ can also result from a texture of the FDCNT composite material. The decrease in the crystallite size could lead to improved electrochemical performance.

![X-ray diffraction patterns](image)

Figure 5.2 X-ray diffraction patterns of (a) mixture of Fe$_3$O$_4$ and CNT prepared without CB and (b) FDCNT (▼-JCPDS file No. 19-0629, ●-JCPDS No. 22-1012).

Raman spectroscopy studies were performed for as-received CNT, synthesized Fe$_3$O$_4$, a mixture of Fe$_3$O$_4$ and CNT, as-received CB and the synthesized FDCNT (Figure 5.3). The Raman spectrum for CNT reveals the in-plane vibration of the C–C bond at 1592 cm$^{-1}$ (G-band), the disordered D-band at 1354 cm$^{-1}$ and G’ band at 2702 cm$^{-1}$ (overtone of D-
band) [31]. The Fe$_3$O$_4$ spectrum shows a peak at ~698 cm$^{-1}$ corresponding to A$_{1g}$ mode [32]. The same bands were observed in the Raman spectrum of the Fe$_3$O$_4$-CNT mixture and FDCNT. The Raman spectra of CB dye is analogous to the different organic dyes with a peak at low wavenumber and multiple peaks in the mid wavenumber range [33, 34]. These peaks were observed in the spectrum of FDCNT and confirmed the incorporation of CB into FDCNT.

Investigations of the effect of Fe$_3$O$_4$/CNT mass ratio ($\gamma$) on the FDCNT morphology and electrochemical properties are important for the optimization of electrode performance. Fe$_3$O$_4$ offers benefits of high capacitance, whereas CNT provide electronic conductivity. The ability to avoid Fe$_3$O$_4$ and CNT agglomeration is critical for the design of composites.

Figure 5.3  Raman spectroscopy data for (a) as-received CNT (b) precipitated Fe$_3$O$_4$, (c) mixture of Fe$_3$O$_4$ and CNT, (d) CB dye, and (d) FDCNT for $\gamma=1.50$.
with enhanced charge storage properties. The STEM images at different magnifications Figure 5.4 (A, B) for FDCNT with $\gamma = 1.5$ show Fe$_3$O$_4$ nanoparticles present on the surface of CNT. The sizes of the nanoparticles are $\sim$20 nm. As $\gamma$ increases to 2.0, the nanoparticles form large agglomerates, as it is evident from Figure 5.4 (C). Energy dispersive X-ray analysis was used to perform line scans on the FDCNT surfaces Figure 5.4 (B). The EDX data Figure 5.4 (D) confirmed the deposition of Fe$_3$O$_4$ on CNT.

Figure 5.4  TEM of FDCNT for different ($\gamma$): (A, B) 1.50, and (C) 2.00. (D) EDX line scan for Fe, the line is shown in (B).
Electrodes prepared without CB showed relatively small CV areas Figure 5.5 A (a, b) indicating low capacitance Figure 5.5 B (a, b). The use of CB as a dispersant resulted in significant increase of the CV areas Figure 5.5 A (c, d) and higher capacitances Figure 5.5 B (c, d). The physical mixing of CNT with Fe$_3$O$_4$ particles, which were dried after chemical precipitation, resulted in relatively low capacitances. The in-situ precipitation of Fe$_3$O$_4$ in the presence of CNT allowed for improved mixing and higher capacitance. FDCNT electrodes, prepared using CB, showed the highest capacitance. Moreover, FDCNT electrodes exhibited lower resistance and higher real part of AC capacitance ($C'_S$) Figure 5.5 (C, D). The AC relaxation frequency, corresponding to the maximum of the imaginary part of AC capacitance $C''_S$, was above 10 mHz Figure 5.5 (E).

The supercapacitor electrodes prepared with CB showed significant capacitance increase in the range of 0 to $-0.5$ V. It is important to note that CB is a redox active material. However, the observed capacitance enhancement cannot be attributed to direct contribution of adsorbed CB to the charge storage due to the redox reaction shown in Figure 5.1 (E). The gravimetric capacitance of CB related to this reaction is very low due to the relatively large mass of CB. Therefore, we suggested that CB additive facilitates charge transfer between Fe$_3$O$_4$ and CNT and allows for better utilization of the charge storage properties of Fe$_3$O$_4$.

It is known that CB is an efficient redox-type charge transfer mediator for electrocatalysis [35], where it is used to shuttle electrons between electrodes and analytes. CB has redox properties Figure 5.1 (E) in a negative potential range and offers benefits of high electron transfer rate constant, excellent reversibility and chemical stability [35].
The chelating bonding of CB to Fe$_3$O$_4$ and electrostatic interactions of CB and Fe$_3$O$_4$ are beneficial for stable redox performance in the negative potential range.

In addition to the redox-type mode of the charge transfer mediation, we also can suggest another mechanism, which can facilitate the charge transfer. This mechanism is related to the catechol-type CB bonding to Fe$_3$O$_4$. Catechol-type molecules are widely used as charge transfer mediators in different fields. In the field of anodic electropolymerization of polypyrrole, catechol-type dopants facilitated charge transfer by creation of bonds to different substrates [36-38] and significantly reduced the anodic electropolymerization potential. As a result, adherent films were obtained on non-noble substrates [36 - 38]. In the field of biosensors and photovoltaic devices the charge transfer complexes [39 - 41] were formed by coordinating catechol with titanium atoms on the TiO$_2$ particle surface. Catechol-type materials are used as electron transfer mediators in advanced sensors [42]. Therefore, we suggested that catechol-type CB bonding could also facilitate charge transfer between Fe$_3$O$_4$ and CNT. The increase in capacitance of FDCNT can result from the ability of CB to facilitate electron transfer by either of two different mechanisms described above.
Figure 5.5. (A) CVs at scan rate of 5 mV s$^{-1}$, (B) $C_S$ and $C_m$ versus scan rate, (C) EIS Nyquist plot, (D) $C_{S'}$ versus frequency and (E) $C_{S''}$ versus frequency for electrodes with $\gamma=1.00$, prepared (a, b) without CB and (c, d) with CB using different methods: (a, c) in-situ chemical precipitation and (b, d) mixing.

The investigation of FDCNT electrodes fabricated with different $\gamma$ provided additional evidence of influence of CB mediated in-situ synthesis on the capacitive behavior. The CV profiles for the electrodes with different $\gamma$ are presented in Figure 5.6 (A-C). The CV area of the electrode with $\gamma=1.5$ is higher than those with $\gamma=1.25$ and $\gamma=2$. The electrode with $\gamma=1.5$ shows Figure 5.6 (D) the highest capacitance of 6.17 F cm$^{-2}$ (154.3 F g$^{-1}$) at 2 mV s$^{-1}$. The retention of capacitance for $\gamma=1.5$ was 37.9 %. The obtained areal capacitance was significantly higher than the literature data for Fe$_3$O$_4$ based electrodes, which were summarized in reviews [2, 43, 44].
Figure 5.6 Testing data for FDCNT electrodes: (A-C) CVs at scan rates of (a) 2, (b) 5, and (c) 10 mV s$^{-1}$ with (A) $\gamma=1.25$, (B) $\gamma=1.50$, and (C) $\gamma=2.00$; (D) $C_s$ and $C_m$ versus scan rate. (E) Nyquist plot of complex impedance and frequency dependences of (F) $C_s'$ and (G) $C_s''$ for D(a), E(a), F(a), G(a) $\gamma=1.25$; D(b), E(b), F(b), G(b) $\gamma=1.50$, and D(c), E(c), F(c), G(c) $\gamma=2.00$. 
The FDCNT electrode with $\gamma = 1.5$ showed the highest capacitance and the highest capacitance retention at different scan rates compared to other electrodes. Galvanostatic charge-discharge was performed on this optimized electrode. The charge-discharge curves at various current densities in (Figure 5.7) (inset) showed nearly symmetrical triangular shapes. The capacitance calculated from the chronopotentiometry data is presented in (Figure 5.7). The highest capacitance of 4.97 F cm$^{-2}$ was obtained at a discharge current of 3 mA cm$^{-2}$.

The fibrous microstructure of the electrode materials and magnetic interactions of Fe$_3$O$_4$ particles facilitated the fabrication of electrodes with relatively low binder content, which was 3% of the total mass of Fe$_3$O$_4$ and CNT. A polymer binder is an important component of the composite electrodes. However, insufficient attention has been paid in the literature to the minimization of binder content in supercapacitor composites. Polymer binders have significantly lower densities than the densities of functional metal oxides. Therefore, volume fractions of binders in composites are high even at relatively low mass concentration of the binders. Many water-insoluble polymers exhibit insulating and hydrophobic properties, which are detrimental for the electrode performance. Therefore, it is important to reduce the volume fraction of the binders in composite electrodes.

The testing results presented above indicate that CB mediated in-situ synthesis produces advanced Fe$_3$O$_4$ based anodes. A similar approach (see the supplementary information) has been utilized to fabricate Mn$_3$O$_4$ based cathodes that showed a capacitance of 5.15 F cm$^{-2}$ at an AM of 40 mg cm$^{-2}$. 

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Figure 5.7  $C_S$ and $C_m$ versus scan rate for FDCNT electrodes with $\gamma=1.50$ obtained from charge-discharge curves (inset) at current densities of (a) 3, (b) 5, (c) 7, and (d) 10 mA cm$^{-2}$.

Spinel based cathodes and anodes, prepared by in-situ precipitation methods using CB were used to fabricate an asymmetric device for operation in a voltage window of 1.6 V. The device exhibited box-type capacitive CV profiles Figure 5.8 (A). The highest areal capacitance obtained for the device was 2.41 F cm$^{-2}$ at 2 mV s$^{-1}$. The capacitance decreased to 0.61 F cm$^{-2}$ at 100 mV s$^{-1}$ with a capacitance retention of 21.5%. The Nyquist plot showed a low impedance. The relaxation frequency of the asymmetric device was lower than that for the individual electrodes. The smaller relaxation frequency can result from higher total resistance of the device than the resistances of the individual electrodes.
Figure 5.8  (A) CVs at scan rates of (a) 2, (b) 5 and (c) 10 mV s$^{-1}$, (B) $C_S$ and $C_m$ versus scan rate, (C) Nyquist plot of complex impedance and frequency dependences of (D) $C_S'$ and (E) $C_S''$ for an asymmetric supercapacitor cell.

The asymmetric device Figure 5.9 (A) displayed ideal triangular shape chronopotentiometry graphs at all current densities in the 3–50 mA cm$^{-2}$ range. The areal capacitance of 2.29 F cm$^{-2}$ was obtained at a current density of 3 mA cm$^{-2}$. The capacitance decreased with current density, the retention at a current density of 50 mA cm$^{-2}$ was 83.3%. The chronopotentiometry graphs were used to calculate the energy density and power density at varied current densities.
Figure 5.9 (B) shows the Ragone plot of the asymmetric device with the highest energy density of 0.91 mWh cm\(^{-2}\) obtained at a current density of 3 mA cm\(^{-2}\) and highest power density of 26.77 mW cm\(^{-2}\) achieved at current density of 50 mA cm\(^{-2}\). The high power-energy density device characteristics were achieved at high AM.

Figure 5.9 (A) Cs and Cm versus charge-discharge rate, obtained from charge-discharge curves (inset) at current densities of (a) 3, (b) 5, (c) 7, (d) 20, (e) 30, (f) 40, and (g) 50 mA cm\(^{-2}\), (B) Ragone plot for an asymmetric supercapacitor cell.

5.5 Conclusions

An asymmetric spinel-spinel supercapacitor has been fabricated using Fe\(_3\)O\(_4\) and Mn\(_3\)O\(_4\) for charge storage in negative and positive electrodes, respectively, and CNT as a conductive additive. High performance of the individual electrodes and devices has been achieved at a high AM of 40 mg cm\(^{-2}\) for the individual electrodes. A conceptually new strategy has been developed, which was based on the use of multifunctional CB dye. CB strongly adsorbed on the spinel phases and CNT, facilitated CNT dispersion, acted as a
capping agent for the synthesis of spinel particles and allowed for the fabrication of spinel
decorated CNT. Moreover, it was discovered that CB is an efficient charge transfer
mediator, which allowed for significant improvement of capacitive behavior. The use of
CB as a charge transfer mediator allowed for good utilization of capacitive properties of
spinels at high AM. The mechanisms of spinel-CB-CNT interactions involved π-π
interactions of CB and CNT and catechol-type chelating bonding of CB with metal atoms
on the spinel particle surface. The charge transfer mediation mechanisms are based on
redox properties of CB and catechol- type bonding. The capacitive properties were
analyzed with cyclic voltammetry, chronopotentiometry and impedance spectroscopy for
the electrodes with different spinel/CNT mass ratios. Areal capacitances of 6.17 and 5.15
F cm\(^{-2}\) were obtained for Fe\(_3\)O\(_4\) and Mn\(_3\)O\(_4\) based electrodes, respectively in 0.5 M Na\(_2\)SO\(_4\)
electrolyte. These high capacitances were achieved at low electrode resistances. The
electrodes were used for the fabrication of an asymmetric device with a capacitance of 2.41
F cm\(^{-2}\) in a voltage window of 1.6 V.

5.6 Declaration of competing interest
The authors declare that they have no known competing financial interests or personal
relationships that could have appeared to influence the work reported in this paper.

5.7 Acknowledgements
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5.8 References


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5.9 Supporting informations

Figure 5.10 (A) CVs at scan rates of (a) 2, (b) 5 and (c) 10 mV s\(^{-1}\), (B) \(C_s\) and \(C_m\) versus scan rate, (C) Nyquist plot of complex impedance and frequency dependences of (D) \(C_s'\) and (E) \(C_s''\). For a positive Mn\(_3\)O\(_4\)-CNT electrode, prepared by precipitation using CB.
Figure 5.11 Charge-discharge curves at current densities of (a) 3, (b) 5, (c) 7, and (d) 10 mA cm$^{-2}$, for a positive Mn$_3$O$_4$-CNT electrode, prepared by precipitation using CB.

Table 5.1 Fe$_3$O$_4$-CNT samples used in this investigation.

<table>
<thead>
<tr>
<th>No.</th>
<th>Mass ratio (γ) Fe$_3$O$_4$-CNT</th>
<th>CB</th>
<th>Synthesis method</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>without</td>
<td>Physical mixing</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>without</td>
<td>In-situ synthesis</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>with</td>
<td>Physical mixing</td>
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<tr>
<td>4</td>
<td>1</td>
<td>with</td>
<td>In-situ synthesis</td>
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<tr>
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<td>In-situ synthesis</td>
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<tr>
<td>6</td>
<td>1.5</td>
<td>with</td>
<td>In-situ synthesis</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>with</td>
<td>In-situ synthesis</td>
</tr>
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Chapter 6

Functionally decorated carbon nanotube networks for energy storage in supercapacitors

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6.1 Abstract

A novel approach has been developed for the fabrication of Fe$_3$O$_4$ decorated multiwalled carbon nanotubes (MWCNT) for energy storage in negative electrodes of electrochemical supercapacitors. Synthesis of Fe$_3$O$_4$ was performed in the presence of MWCNT, dispersed using various cationic and anionic polyaromatic dispersants. The comparison of experimental results obtained using different dispersants provided an insight into the influence of the chemical structure of the dispersant molecules on the microstructure of the Fe$_3$O$_4$-MWCNT materials. It was found that positively charged groups and chelating catechol ligands of the dispersants facilitated the formation of Fe$_3$O$_4$ decorated MWCNT with low agglomeration. The Fe$_3$O$_4$-MWCNT materials, prepared using different dispersants were used for the fabrication of electrodes with mass loading of 40 mg cm$^{-2}$. The highest capacitance was obtained in 0.5 M Na$_2$SO$_4$ electrolyte for Fe$_3$O$_4$ decorated MWCNT prepared using cationic celestine blue dye as a dispersant. Improved cyclic voltammetry profile was obtained using FeOOH as an additive. Asymmetric devices were fabricated and tested based on the Fe$_3$O$_4$ decorated MWCNT negative electrodes and MnO$_2$-MWCNT positive electrodes.

Keywords: carbon nanotube, iron oxide, energy, supercapacitor, dispersant
6.2 Introduction

Electrochemical supercapacitors are currently under intensive investigation for energy storage and capacitive water purification applications (Shi et al., 2014; Zhao and Zheng, 2015; Ding et al., 2020). Research is focused on the development of new materials and electrolytes (Brousse & Bélanger, 2003; Shi & Zhitomirsky, 2010; Li et al., 2019), fabrication of nanoparticles of active materials (Luo et al., 2016; Silva et al., 2018), design and modeling of composite electrodes and devices (Pavaskar et al., 2018; Xing et al., 2019). New strategies have been designed for the fabrication of carbon based electrodes with enhanced capacitive performance (Salinas Torres et al., 2019). Significant interest has been generated in application of carbon nanotubes (CNT) for the fabrication of composite electrode materials (Lu et al., 2019). The interest in CNT applications for supercapacitors is related to high electronic conductivity and high surface area of CNT.

It was recognized that CNT can be decorated with other functional materials (Pan et al., 2015; Hao et al., 2016). With a desire to fabricate new and advanced devices, there is growing interest in the development of new techniques for the fabrication of functionally decorated CNT, such as laser ablation (Imbrogno et al., 2017), atomic layer deposition (Ding et al., 2018), polymerization (Zhu et al., 2014), magnetron sputtering (Wei et al., 2014), electrodeposition (Chitturi et al., 2016), and chemical precipitation (Hong et al., 2013). Decorated CNT are of particular interest for energy storage and generation devices, such as supercapacitors, batteries and fuel cells.
The use of functionally decorated CNT allowed for the fabrication of advanced batteries with enhanced capacity (Hong et al., 2013; Wei et al., 2014), good cyclic stability (Chitturi et al., 2016) and improved conductivity (Wang et al., 2010). It has been reported that CNT can be decorated with catalysts for advanced application in fuel cells (Sonkar et al., 2017). Significant advances have been achieved in applications of functionally decorated CNT for photovoltaic devices (Mathew et al., 2011; Tai et al., 2014). It has previously been shown that carbon nanotubes can be decorated with oxides (Ojha et al., 2019), polypyrrole (Su & Zhitomirsky, 2015) and activated carbon (Shi et al., 2014) for energy storage applications in supercapacitors.

Previous studies highlighted the need in the development of efficient manufacturing techniques for the fabrication of functionally decorated CNT. Such techniques need to be based on the careful selection of dispersing agents, which must be well adsorbed on the CNT surface. Good dispersion of CNT is critical for their decoration with functional materials. The use of networks of decorated CNT is promising for the fabrication of advanced supercapacitor electrodes with high active mass.

The objective of this investigation was the fabrication of Fe₃O₄ decorated CNT for application in negative electrodes of asymmetric supercapacitors. Following this objective, we investigated anionic and cationic aromatic dispersants for the dispersion of CNT. The results presented below indicated that chemical precipitation of Fe₃O₄ in the presence of CNT allowed for the fabrication of Fe₃O₄ decorated CNT. Testing results provided an insight into the influence of electric charge and chelating groups of the dispersants on the Fe₃O₄ formation on the CNT surface. The fibrous networks of decorated CNT were used
for the fabrication of negative electrodes with high active mass of 40 mg cm\(^{-2}\). The capacitive behavior was linked to dispersant structure. Finally, we fabricated and tested an asymmetric supercapacitor device.

6.3 Experimental procedures

Iron (II) chloride tetrahydrate (FeCl\(_2\)·4H\(_2\)O), iron (III) chloride hexahydrate (FeCl\(_3\)·6H\(_2\)O), ammonium hydroxide (NH\(_4\)OH), sodium hydroxide (NaOH), sodium sulfate (Na\(_2\)SO\(_4\)), Palmetic acid (PA), celestine blue (CB), pyrocatechol violet (PV), azure A chloride (AA), m-cresol purple (CP), poly(vinyl butyral-co-vinyl-alcohol-co-vinyl-acetate) (PVB, average MW = 50,000-80,000), multiwalled carbon nanotubes (MWCNT, purity > 95\%, OD 20-30 nm, and length 1–2 \(\mu\)m, US Nanomaterial Inc, USA), and Ni foam (porosity of 95\%, Vale Ltd., Canada) were used.

For decoration of the MWCNT by Fe\(_3\)O\(_4\) nanoparticles, the synthesis of the nanoparticles was performed in the presence of dispersed MWCNT. In this procedure, 1 g L\(^{-1}\) of MWCNT were dispersed in DI water by ultrasonication for 15 min and then 0.25 g L\(^{-1}\) dispersant was added and suspension was ultrasonicated again for 15 min. A stoichiometric mixture of Fe\(^{2+}\) and Fe\(^{3+}\) salts dissolved in DI water was added to the suspension of MWCNT in order to obtain the mass ratio of Fe\(_3\)O\(_4\) to MWCNT equal to 1.5. The pH was adjusted to 9 by the addition of 1 M NH\(_4\)OH. The obtained suspension was ultrasonicated for 40 min and then filtrated. The materials were washed with DI water and dried overnight. The magnetite decorated MWCNT, prepared using CB, PV, AA and CP were denoted as M-CB-MWCNT, M-PV-MWCNT, M-AA-MWCNT and M-CP-MWCNT, respectively. Non-agglomerated FeOOH nanoparticles were
prepared by a chemical precipitation and liquid-liquid extraction method (Chen et al., 2019). However, in contrast to the previous investigation (Chen et al., 2019) PA was used as a new and efficient extractor. M-FH-CB-MWCNT material was prepared by mixing of M-CB-MWCNT (80%) and FeOOH (20%).

M-CB-MWCNT, M-PV-MWCNT, M-AA-MWCNT, M-CP-MWCNT and M-FH-CB-MWCNT were dispersed in ethanol, containing dissolved PVB binder and obtained slurries were used for the impregnation of Ni foam current collectors and fabrication of negative electrodes of supercapacitors. The PVB binder content in the electrodes was 3%. The total mass of the impregnated material was 40 mg cm\(^{-2}\). MnO\(_2\)-MWCNT material for positive electrodes was prepared by the precipitation and liquid-liquid extraction method (Chen, et al., 2017). The asymmetric device was fabricated containing M-FH-CB-MWCNT negative electrodes with mass loading of 40 mg cm\(^{-2}\) and MnO\(_2\)-MWCNT positive electrodes with mass loading of 35 mg cm\(^{-2}\). At such mass loadings the capacitance of negative electrodes matched the capacitance of the positive electrodes.

Transmission electron microscopy was performed (dark field STEM) using a JEOL 2010F field emission microscope. X-ray diffraction (XRD) analysis was performed using the Bruker D8 Discover instrument comprising Davinci diffractometer and Co-K\(\alpha\) radiation. Particle size distribution was done using dynamic light scattering (DLS) model (DelsaMax Pro- Beckman Coulter). The analysis was carried out based on testing of 4 sets of each material with a concentration of 0.4 mg L\(^{-1}\) in DI, where every set consisted of 10 acquisition.
Cyclic voltammetry and electrochemical impedance spectroscopy studies of single electrodes and asymmetric device were performed in 0.5 M Na$_2$SO$_4$ electrolyte as described in prior investigations (Shi & Zhitomirsky, 2013; Zhu et al., 2014; Chen et al., 2017). EIS measurements were carried out in the frequency range of 10 mHz−100 kHz with a sinusoidal signal of 10mV. The components of complex capacitance ($C'_s$ and $C''_s$) were calculated from the EIS data as $C'_s = \frac{Z''}{\omega|Z|^2}$ and $C''_s = \frac{Z'}{\omega|Z|^2}$, where $\omega = 2\pi f$ and $f$ is frequency. Galvanostatic charge−discharge of individual electrodes at different current densities and discussion was performed using Biologic VMP300 potentiostat. The charge-discharge behavior of the asymmetric device was analyzed using battery analyzers BST8-MA and BST8-3 (MTI Corporation, USA).

6.4 Results and discussion

Figure 6.1 (A) shows chemical structures of aromatic dispersants used for dispersion of MWCNT. The polyaromatic structure of the dispersants was beneficial (Ata et al., 2018) for their adsorption on MWCNT. The adsorption mechanism involved π-π interactions. The adsorbed dispersants imparted a positive charge (CB, AA) or a negative charge (PV, CP) to MWCNT. The small size, electric charge and good adsorption of the dispersants on MWCNT facilitated MWCNT dispersion by unzipping mechanism (Ata et al., 2018; Figure 6.1 (E)) and allowed for the fabrication of stable suspensions. Figure 6.1 (F, G) illustrates different types of interactions of the dispersants with Fe$_3$O$_4$ particles. The precipitation of Fe$_3$O$_4$ was achieved at pH=9, which is above the isoelectric point (pH=6.5) (Parks, 1965) of this material.
Therefore, the Fe$_3$O$_4$ particles were negatively charged. The negative charge of Fe$_3$O$_4$ resulted in electrostatic repulsion of Fe$_3$O$_4$ and anionic PV or CP, adsorbed on MWCNT Figure 6.1 (F). In contrast, electrostatic attraction existed between Fe$_3$O$_4$ and cationic CB or AA molecules, adsorbed on MWCNT Figure 6.1 (G). Previous investigations (Ata et al., 2014) showed that molecules, containing a catechol group, strongly adsorbed on inorganic particles and facilitated their efficient dispersion. Therefore, CB and PV can be adsorbed on Fe$_3$O$_4$ particles by catecholate type bonding. Figure 6.1 (F) shows bonding of PV to the Fe atom on the particle surface. A similar mechanism can be suggested for CB bonding. It is important to note that phenolic molecules containing single OH groups, such as CP, show poor adsorption on inorganic molecules (Ata et al., 2014). In contrast, molecules from the catechol family, such as PV, containing two adjacent OH groups, show very strong bonding to the inorganic particles (Ata et al., 2014).

X-ray diffraction studies confirmed the formation of pure Fe$_3$O$_4$ by precipitation from mixed Fe$^{2+}$ and Fe$^{3+}$ salt solutions (supplementary information, Figure 6.10). The materials prepared by precipitation from the same solutions, containing dispersed MWCNT, showed X-ray diffraction peaks of Fe$_3$O$_4$ and MWCNT (Figure 6.2). Peak broadening resulted from the small particle size of Fe$_3$O$_4$. 

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Figure 6.1 Chemical structures of (A) CB, (B) PV, (C) AA, (D) CP and schematics, showing (E) unzipping of MWCNT bundles by dispersants, (F) electrostatic repulsion of PV and Fe₃O₄ particles and chelating bonding of PV to Fe atoms on the Fe₃O₄ particle surface, involving a catechol group of PV, (G) electrostatic attraction of AA and Fe₃O₄.
Figure 6.3 shows TEM images of the materials at different magnifications. The TEM images of M-CBMWCNT showed the formation of Fe$_3$O$_4$ decorated MWCNT. The size of the Fe$_3$O$_4$ particles adsorbed on the MWCNT was about 10 nm. It is suggested that electrostatic attraction of positively charged CB dispersant and negatively charged Fe$_3$O$_4$ as well as chelating bonding of the catechol group facilitated the formation of the decorated MWCNT. It is important to note that electrostatic repulsion of the PV dispersant, adsorbed on the MWCNT surface, and Fe$_3$O$_4$ nanoparticles was detrimental for the formation of the decorated MWCNT. On the other hand, the chelating bonding of the catechol groups of PV promoted Fe$_3$O$_4$ formation on the MWCNT surface. The chelating bonding was a dominating mechanism, which allowed for the formation of decorated MWCNT. However, the TEM studies of M-PV-MWCNT also revealed the formation of small agglomerates of the Fe$_3$O$_4$ particles as it is shown in Figure 6.3 (F).
The analysis of the TEM images for M-AA-MWCNT and M-CP-MWCNT showed enhanced agglomeration of the Fe$_3$O$_4$ particles. The agglomeration is especially evident for M-CP-MWCNT samples. In this case, the poor coverage of MWCNT resulted from electrostatic repulsion of CP and Fe$_3$O$_4$.

The effect of different dispersing agents has also been studied using DLS analysis (Figure 6.4). The size distribution of the aggregates in all samples is bimodal with different degree of polydispersity. The effect of different dispersing agents has also been
studied using DLS analysis (Figure 6.4). The size distribution of the aggregates in all samples is bimodal with different degree of polydispersity. The first peak at ~100 nm is present in all four dispersions with different intensities. The second peak was observed in the range of $10^3$-$10^4$ nm. The intensity and polydispersity of the second peak are smallest for M-CB-MWCNT. The polydispersity of M-PV-MWCNT is broader than that of M-CB-MWCNT. The analysis of the DLS data for M-AA-MWCNT and M-CP-MWCNT revealed significant increase in the relative intensity of the second peak, compared to the intensity of the first peak. The second peak for M-AA-MWCNT and M-CP-MWCNT shifted to larger radius numbers, compared to the second peak for M-CB-MWCNT. The increase in relative intensity of the second peak for M-AA-MWCNT and M-CP-MWCNT and peak shifts indicated an increasing number of agglomerates and increase in the agglomerate size of the particles.

Figure 6.4  (A) Average data (40 samples of each composition) for DLS analysis of (a) M-CB-MWCNT, (b) M-PV-MWCNT, (c) M-AA-MWCNT and (d) M-CP-MWCNT, (B) Typical spectrum for M-CP-MWCNT. The width of the peaks indicates the polydispersity of the aggregate (Pd).
This is in agreement with the TEM data and indicates the beneficial effect of the catechol groups of CB and PV for the formation of decorated CNT and reduction of Fe₃O₄ agglomeration. It is important to note that the decoration of MWCNT resulted from the dispersant mediated adsorption. In this approach the changes in MWCNT structure, resulting from chemical reactions and high temperature treatment (Xing et al. 2015, 2017, 2019) can be avoided.

M-CB-MWCNT, M-PV-MWCNT, M-AA-MWCNT, M-CP-MWCNT were used for the fabrication of supercapacitor electrodes with mass loading of 40 mg cm⁻². Figure 6.5 shows cyclic voltammetry data for the electrodes in the potential range of -0.9 - 0.0 V vs. SCE. M-CB-MWCNT electrodes showed a larger CV area, compared to other electrodes and higher integral capacitance in the selected potential window. The M-CP-MWCNT electrodes showed lower capacitance, compared to other materials. The higher capacitance of M-CB-MWCNT can result from reduced agglomeration of the Fe₃O₄ particles and improved contact of Fe₃O₄ and MWCNT. However, the CV for M-CB-MWCNT showed redox peaks and deviated significantly from the box shape. Significant reduction of the charge and discharge currents was observed in the potential range of -0.4 to -0.7V. The observed redox peak can result from the redox-active properties of CB (Noorbakhsh et al., 2008). Such CV shape is detrimental for the fabrication of asymmetric cells. In order to improve the CV profile, M-CB-MWCNT was combined with FeOOH, which shows good charge storage properties in the range of -0.4 to -0.7 V (Chen et al., 2018). Therefore, M-FH-CB-MWCNT was prepared and tested. This material showed improved CV shape, compared to M-CB-MWCNT. The capacitance of 5.76 F cm⁻² (144 F g⁻¹) was obtained at a scan rate of 2 mV s⁻¹.
Figure 6.5  (A,C) CVs and (B,D) capacitance vs. scan rate for (a) M-CB-MWCNT, (b) M-FH-CB-MWCNT, (c) M-PV-MWCNT, (d) M-AA-MWCNT and (e) M-CP-MWCNT electrodes.

Figure 6.6 shows frequency dependences of the components of differential AC capacitance, calculated from the impedance data. M-CB-MWCNT showed the highest real part of capacitance $C'_S$ at low frequencies, compared to other materials. However, the M-FH-CB-MWCNT electrodes showed lower $C''_S$, which indicated lower energy losses. The slightly higher relaxation frequency, corresponding to maximum of $C''_S$, indicated better performance. The M-CP-MWCNT electrodes, showed lower $C'_S$ and lower relaxation frequency, compared to other materials. The capacitive behavior of the electrodes has also been analyzed by chronopotentiometry.
Figure 6.6 (A–D) Frequency dependences of components of complex AC capacitance, calculated from impedance data for (a) M-CB-MWCNT, (b) M-FH-CB-MWCNT, (c) M-PV-MWCNT, (d) M-AA-MWCNT and (e) M-CP-MWCNT electrodes.

Figure 6.7 compares galvanostatic charge-discharge curves for different electrodes and capacitances, calculated from the discharge data at different current densities. The charge-discharge curves were of nearly triangular shape. The highest capacitance at 3 mA cm\(^{-2}\) was achieved using M-CP-MWCNT. However, M-FH-CB-MWCNT showed benefits of nearly constant capacitance in the range of 3-10 mA cm\(^{-2}\). The M-CP-MWCNT and M-FH-CB-MWCNT electrodes showed practically the same capacitances at 5 and 10 mA cm\(^{-2}\). The M-CP-MWCNT electrodes showed significantly lower capacitance, compared to other electrodes in agreement with CV and impedance spectroscopy data.
Figure 6.7  (A) Charge-discharge curves at current density of 5mA cm\(^{-2}\), (B) capacitance, calculated from charge-discharge data, vs. current density for (a) M-CB-MWCNT, (b) M-FH-CB-MWCNT, (c) M-PV-MWCNT, (d) M-AA-MWCNT and (e) M-CP-MWCNT.

M-FH-CB-MWCNT electrodes were used for the fabrication of the asymmetric supercapacitor cells. One of the problems related to the fabrication of asymmetric devices with Na\(_2\)SO\(_4\) electrolyte is related to lower capacitance of negative electrodes, compared to the capacitance of advanced positive electrodes, such as MnO\(_2\)-MWCNT (Ri Chen et al., 2017). However, M-FH-CB-MWCNT electrodes showed relatively high capacitance and the asymmetric device was fabricated using 40 mg cm\(^{-2}\) M-FH-CB-MWCNT negative electrode and 35 mg cm\(^{-2}\) MnO\(_2\)-MWCNT positive electrode. Figure 6.8 (A) shows CVs for the device in a voltage window of 1.6 V. The current increased with increasing scan rate. As expected, the capacitance C\(_S\) of the device was about 50% of the capacitance of the individual electrodes Figure 6.8 (B). The device showed relatively low impedance and relatively high relaxation frequency Figure 6.8 (C-E).
Figure 6.8  (A) CVs at scan rates of (a) 2, (b) 5 and (c) 10 mV s\(^{-1}\), (B) \(C_S\) and \(C_m\) calculated from the CV data versus scan rate, (C) Nyquist plot of complex impedance and frequency dependences of (D) \(C_s'\) and (E) \(C_s''\) for an asymmetric supercapacitor cell, containing M-FH-CB-MWCNT as a negative electrode and MnO\(_2\)-MWCNT as a positive electrode.

The asymmetric devices showed ideal triangular shape charge-discharge curves Figure 6.9 (A, inset). The capacitance slightly decreased Figure 6.9 (A) with current density in the range of 3-50 mA cm\(^{-2}\). The capacitance retention after 1000 cycles was 75% Figure 6.9 (B). The Coulombic efficiency remained about 100% during cycling. The device had an energy density of about 1 mWh cm\(^{-2}\) which showed relatively small variations with increasing current density in the range of 3-50 mA cm\(^{-2}\) Figure 6.9 (C). Two cells, connected in series, allowed for the powering of eleven 20 mA LEDs, as it is shown in Figure 6.9 (D).
Figure 6.9 (A) $C_S$ and $C_m$ vs. current density calculated from discharge data, inset shows charge-discharge curves, and different current densities, (B) (a) Coulombic efficiency and (b) capacitance retention and vs. cycle number, (C) Ragone plot for an asymmetric supercapacitor cell, containing M-FH-CB-MWCNT as a negative electrode and MnO$_2$-MWCNT as a positive electrode, (D) LEDs powered by two asymmetric cells.

6.5 Conclusions

Polyaromatic CB, PV, AA and CP molecules allowed for efficient dispersion of MWCNT. The chelating catechol groups of CB and PV as well as electrostatic attraction of cationic CB and AA with negatively charged Fe$_3$O$_4$ particles were beneficial for the formation of Fe$_3$O$_4$ decorated MWCNT. M-CB-MWCNT showed a network of Fe$_3$O$_4$ decorated
MWCNT and low agglomeration of Fe$_3$O$_4$ nanoparticles. M-CB-MWCNT exhibited higher capacitance, compared to M-PV-MWCNT, M-AA-MWCNT and M-CP-MWCNT. Compared to M-CB-MWCNT, the M-FH-CB-MWCNT electrodes showed improved CV profile, reduced AC energy losses and low variation of capacitance with increasing charge-discharge current. M-FH-CB-MWCNT showed good capacitive behavior at mass loading of 40 mg cm$^{-2}$. Asymmetric devices were fabricated, containing M-FH-CB-MWCNT negative electrodes and MnO$_2$-MWCNT positive electrodes, which showed promising capacitance and power-energy characteristics.

6.6 Author contributions

MN conducted synthesis of materials, performed materials characterization and electrochemical testing and contributed to the writing of the manuscript. RS contributed to DLS and electron microscopy testing, data analysis and writing of the manuscript. IZ contributed to the development of new dispersants, cell design, and IP and IZ contributed to the data analysis and writing of the manuscript.

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6.8 Acknowledgment

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Facility for XRD for assistance with measurements, and Dr. R. Poon for fruitful discussions and technical support.

6.9 Data availability statement

The datasets generated for this study are available on request to the corresponding author.

6.10 Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

6.11 Supplementary material

The supplementary material for this article can be found online at https://www.frontiersin.org/articles/10.3389/fenrg.2020.0004/full/supplementarymaterial
6.12 References


6.13 Supporting informations

Figure 6.10 X-ray diffraction patterns of Fe$_3$O$_4$ powder (JCPDS file 19-0629).
Table 6.1  Detailed results for CVs, the average $C_s$, $C_m$ versus scan rates capacitance vs. scan rate for (a) M-CB-MWCNT, (b) M-FH-CB-MWCNT, (c) M-PV-MWCNT,(d) M-AA-MWCNT and (e) M-CP-MWCNT electrodes.

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Table 6.2  Detailed results for GCD, the average $C_s$, $C_m$ versus scan rates capacitance vs. scan rate for (a) M-CB-MWCNT, (b) M-FH-CB-MWCNT, (c) M-PV-MWCNT,(d) M-AA-MWCNT and (e) M-CP-MWCNT electrodes.

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Chapter 7

Pseudocapacitive behavior of ferrimagnetic NiFe$_2$O$_4$-carbon nanotube electrodes prepared with a multifunctional dispersing agent.

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7.1 Abstract

We investigate the pseudocapacitive properties of ferrimagnetic NiFe$_2$O$_4$ ceramics in a 0.5 M Na$_2$SO$_4$ aqueous electrolyte. These ceramics have a high capacitance of 2.33 Fcm$^{-2}$ since a more efficient colloidal technique is applied, which enhances the current response of the electrode in the negative potential range. NiFe$_2$O$_4$ is co-dispersed with multiwalled carbon nanotubes (MWCNTs) using Celestine Blue (CB) dye as a multifunctional co-dispersant. The capacitance measurements are performed by cyclic voltammetry, impedance spectroscopy and galvanostatic charge-discharge. The experiments reveal the synergistic effects of NiFe$_2$O$_4$ and conductive MWCNTs additives and the benefit they provide through co-dispersion with CB, which acts as an electron transfer mediator, enhancing pseudocapacitance. The mass ratio of NiFe$_2$O$_4$ and MWCNTs in the composite electrodes is varied to optimize the capacitance enhancement, lower electrical resistance at a high active mass loading of 40 mg cm$^{-2}$, and achieve favorable capacitance retention at high charge-discharge rates. The results reveal a path for the development of pseudocapacitive ferrimagnetic ceramic composites that have advanced functionality.

Keywords: pseudocapacitance, ferrimagnetic, spinel, dispersant, charge transfer, dye
7.2 Introduction

The combination of the magnetic and electrical capacitive properties of ceramic materials offers the potential to develop many novel applications in multifunctional devices. The discovery [1-3] of magnetically ordered ferroelectrics or multiferroics has generated interest in materials that combine the magnetic ordering with a high capacitance that result from spontaneous ferroelectric polarization due to the influence of the magnetic field on material electrical properties and vice versa [4]. However, the relatively high conductivity of some magnetically ordered ferroelectrics limits the occurrence of magnetocapacitive effects at room temperature, but here investigations of the pseudocapacitive properties of magnetic materials [5-7] and multiferroics [8] have revealed a new research avenue. Pseudocapacitive materials exhibit superior electrical capacitance [9-11] compared to that of ferroelectric materials. The capacitance of pseudocapacitors is typically by 6-8 orders of magnitude higher [12] than of ferroelectric capacitors of the same mass. Ideal pseudocapacitive and ferroelectric materials exhibit rectangular current-voltage dependences at low voltages [12, 13]. However, the origin of this pseudocapacitance is different from that of ferroelectric dipole capacitance. Pseudocapacitive properties of materials result from fast reversible redox reactions [14]. Therefore, in contrast to ferroelectric materials, a high material conductivity is an important beneficial factor for efficient pseudocapacitive charge-discharge [12]. Pseudocapacitors can operate at low voltages. In contrast, higher voltages can be applied to ferroelectric materials. However, the dielectric constant and capacitance of ferroelectric materials decreases drastically with increasing voltage. Moreover, the current-voltage characteristics of ferroelectric
capacitors at high voltages can deviate significantly from ideal capacitive rectangular shapes due to various polarization switching phenomena. The dielectric constant of ferroelectric materials decreases with decreasing crystal size to the nanometer scale. In contrast, the pseudocapacitance increases with decreasing particle size and increasing surface area. The use of nanoparticles with the high surface area is crucial to utilize high theoretical pseudocapacitance of suitable materials for practical applications.

The materials science of magnetically ordered pseudocapacitors (MOPC) is an emerging field of technological and scientific interest [6, 15, 16]. Of particular importance are ferrimagnetic MOPC ceramic materials, such as spinels [17-19] and hexagonal ferrites [20], which exhibit high magnetization at room temperature. MOPC materials can have enhanced charge storage properties induced by magnetic fields [21, 22]. However, the mechanism of this pseudocapacitance increase under the influence of a magnetic field is not well understood. Investigations of paramagnetic Mn₃O₄ at room temperature have shown that the pseudocapacitance is reduced under the influence of a magnetic field [22]. The fabrication of pseudocapacitive electrodes that are influenced by magnetic fields offers a unique opportunity to manipulate microstructure design to improve their pseudocapacitive behavior [23-25]. Significant progress has been made in the magnetic field-assisted preparation of advanced pseudocapacitors based on paramagnetic oxides [23-25]. However, strong magnetic interactions between particles of ferrimagnetic MOPC can enhance nanoparticle agglomeration and diminish mixing with conductive additives, which is detrimental for pseudocapacitive performance. There is significant interest in NiFe₂O₄ spinel, which has ferrimagnetic ordering and high dielectric constant [26-29]. Previous
investigations have focused on the fabrication of NiFe$_2$O$_4$-based multiferroic composites with high capacitance [30-33] and magnetocapacitive thin film devices [34-36]. Other investigations showed that NiFe$_2$O$_4$ is a promising MOPC material, where its pseudocapacitive behavior in KOH electrolytes has a relatively high capacitance in both positive and negative potential windows [37, 38]. Enhanced capacitive behavior in KOH electrolytes has been reported for various NiFe$_2$O$_4$ based composites, containing graphene [39, 40], reduced graphene oxide [41], SiO$_2$ [42], NiO [43], activated carbon [44, 45], and layered double hydroxides [46]. The literature describes the pseudocapacitive properties of NiFe$_2$O$_4$ based composites in H$_2$SO$_4$ [47, 48], KNO$_3$ [49], NaCl [50], and gel electrolytes [51-53]. The capacitive behavior in an Na$_2$SO$_4$ electrolyte is of particular interest for fabricating asymmetric capacitors with an enlarged voltage window. While the promising behavior of this arrangement is known [54], investigations have been limited to electrodes with the relatively low active mass [55, 56] of 5 mg cm$^{-2}$. Superior electrode performance must be achieved at high active mass for electrodes with high areal capacitance ($C_S$) and low resistance. The goal of this investigation was to fabricate advanced NiFe$_2$O$_4$ based composites containing carbon nanotubes as conductive additives for operation in an Na$_2$SO$_4$ electrolyte. We used a multifunctional co-dispersing agent to disperse the NiFe$_2$O$_4$ and carbon nanotubes, which reduced the agglomeration of NiFe$_2$O$_4$ and carbon nanotubes. The better co-dispersion facilitated greater mixing of these components and thus allowed the fabrication of high active mass electrodes with higher areal capacitance and lower resistance. The redox-active dispersant acted as a charge transfer agent, which enhanced the MOPC NiFe$_2$O$_4$ electrical response.
7.3 Experimental procedures

Celestine blue dye (CB), NiFe$_2$O$_4$ (particle size $<$100 nm), Na$_2$SO$_4$, ethanol, poly(vinyl butyral-co-vinyl-alcohol-co-vinyl-acetate) (PVB, average MW = 50,000-80,000), multiwalled carbon nanotubes (MWCNTs, purity $>$ 95 %, OD 20-30 nm, and length 1–2 μm, US Nanomaterial Inc, USA), and Ni foam (porosity of 95%, Vale Ltd., Canada) were used.

Mixtures of NiFe$_2$O$_4$ and MWCNTs with different mass ratios $\gamma$ (NiFe$_2$O$_4$/MWCNTs) = 1, 1.5, 2.5, and 4 in DI water were prepared and CB was added as a dispersant. Due to the low density and high aspect ratio of MWCNTs, we were not able to impregnate more than 20 mg cm$^{-2}$ MWCNTs into the commercial Ni foam current collectors. Therefore, in order to compare electrode performance at the same total mass loadings (40 mg cm$^{-2}$), the NiFe$_2$O$_4$/MWCNTs mass ratio was changed in a limited range of 1-4. The mass of the added CB was 15 % of the total mass of NiFe$_2$O$_4$ and MWCNTs. The CB content was optimized at the level of 15% in order to achieve good colloidal stability at a minimum dispersant content in the colloidal suspension. The resulting mixture was ultrasonicated, filtrated, washed with DI water to remove non-adsorbed CB, and redispersed in ethanol by ultrasonic agitation. NiFe$_2$O$_4$ and MWCNTs with different $\gamma$ were also dispersed by ultrasonic treatment in ethanol without the use of a dispersant. PVB binder was added to the suspensions, the amount of PVB was 3% of the total mass of NiFe$_2$O$_4$ and MWCNTs. The suspensions of NiFe$_2$O$_4$ and MWCNTs in ethanol containing dissolved PVB were used for the impregnation of commercial Ni foam current collectors.
Transmission Electron Microscopy (TEM) was performed using a JEOL 2010F field emission microscope. Elemental analysis was performed using EDX by line and mapping analysis. X-ray diffraction (XRD) analysis was performed using a Bruker D8 DISCOVER instrument comprising DAVINCI diffractometer and Co-Kα radiation. FTIR measurements were carried out on a Bruker Vertex 70 spectrometer in the wavenumber range of 400 - 2000 cm$^{-1}$.

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) studies of single electrodes were performed as described in prior investigations [14]. Galvanostatic charge-discharge (GCD) was performed using Biologic VMP 300 at current densities of 3 - 40 mA cm$^{-2}$. Areal capacitances ($C_s$) and gravimetric capacitances ($C_m$) were calculated from the CV, GCD, and EIS data, as described elsewhere [12].

### 7.4 Results and discussion

We have developed a facile approach to fabricate NiFe$_2$O$_4$-MWCNTs composite electrodes that have enhanced pseudocapacitive performance by addressing issues related to composite design by using CB as a multifunctional dispersing agent. The major difficulty in utilizing NiFe$_2$O$_4$ nanoparticles for supercapacitors is related to particle agglomeration, which results not only from the Van der Waals attraction forces but also from strong magnetic interactions. Therefore, ferrimagnetic NiFe$_2$O$_4$ nanoparticles must be well-dispersed using a superior dispersant. Another obstacle for NiFe$_2$O$_4$ application in supercapacitors is related to the low conductivity of this material. Therefore, conductive additives, such as MWCNTs, must be added to NiFe$_2$O$_4$ to format nanocomposites with enhanced electronic conductivity. MWCNTs are prone to strong agglomeration due to their
hydrophobic interactions. Therefore, the use of dispersant that co-disperses \( \text{NiFe}_2\text{O}_4 \) and MWCNTs is critical for their good mixing. High charge transfer resistance is another factor, limiting charge transfer between redox-active materials, conductive additives, and current collectors. These problems were addressed by using CB as a multifunctional catecholate molecule. The selection of CB as a dispersant was motivated by various considerations, as described below. Catecholate molecules are gaining attention as efficient dispersants for inorganic nanoparticles. The basis for using catecholates [57] in the colloidal processing of inorganic nanomaterials comes from the investigation of super-strong mussel adsorption on inorganic materials, which involves the bonding of chelating catechol monomers of their proteins to surface metal atoms. Catecholate molecules are of particular interest for the surface modification of magnetic nanoparticles. Catecholate adsorption on magnetic nanoparticles restores the structure and magnetic properties of the surface magnetically dead layer, resulting in enhanced particle magnetization and an increase in the superparamagnetic blocking temperature [58, 59]. The \( \text{NiFe}_2\text{O}_4 \) and MWCNTs suspensions prepared using CB as a dispersant had enhanced colloidal stability compared to suspensions prepared without CB. Sedimentation tests showed that the \( \text{NiFe}_2\text{O}_4 \) and MWCNTs suspensions in ethanol were stable for more than 4 days.

Figure 7.1 shows a chemical structure of CB, which is a cationic polyaromatic molecule, containing a catechol group. The greater colloidal stability of the suspensions results from CB adsorption on \( \text{NiFe}_2\text{O}_4 \) and MWCNTs. The CB adsorption on \( \text{NiFe}_2\text{O}_4 \) occurs due to chelating bonding of the catechol group Figure 7.1 (B), whereas \( \pi-\pi \)
interactions promote CB adsorption on MWCNTs. Similar to other small aromatic dispersants, CB facilitates MWCNTs dispersion via the unzipping mechanism [60]. The adsorbed CB imparts a positive charge to NiFe\(_2\)O\(_4\) and MWCNT for the electrostatic dispersion, which improves their mixing in the composite electrode Figure 7.1 (C).

Figure 7.1 (A) Chemical structure of cationic CB, containing a chelating catechol group (B) interaction of CB with NiFe\(_2\)O\(_4\) particles: chelating bonding with M (Ni, Fe), and (C) unzipping mechanism of MWCNTs dispersion using CB, decoration of MWCNTs and NiFe\(_2\)O\(_4\) by CB interaction with both materials.

Figure 7.2 shows X-ray diffraction patterns of a mechanical mixture of NiFe\(_2\)O\(_4\) with MWCNTs and a NiFe\(_2\)O\(_4\)-MWCNTs (γ=1) composite prepared using CB as a co-dispersant. The diffraction peaks correspond to JCPDS files of spinel NiFe\(_2\)O\(_4\) phase (file 74-1913) and MWCNTs (file 22-1012).
Figure 7.2 X-ray diffraction patterns of (a) mixture of NiFe$_2$O$_4$ with MWCNTs and (b) NiFe$_2$O$_4$-MWCNTs composite, prepared using CB for $\gamma$ = 1 in comparison with JCPDS file 22-1012 and 74-1913.

The FTIR spectrum of the NiFe$_2$O$_4$-MWCNTs ($\gamma$=1) composite shows absorptions, which is not observed in the spectrum of the mechanical mixture (Figure 7.3). These absorptions are attributed to the adsorbed CB. The absorptions at 1550, 1450, and 1390 cm$^{-1}$ result from the stretching of aromatic rings $\nu$(C=C) and $\nu$(C=) [61]. Small peaks at 1345 and 1325 cm$^{-1}$ are attributed to $\nu$(C=N) and $\nu$ C=N) stretching vibrations [61]. The absorptions at 1255 and 1215 cm$^{-1}$ represent C=O and C=O vibrations, respectively [62]. The absorption at 1175 cm$^{-1}$ results from aryl oxygen stretching [63]. The bands at 1110 and 1072 cm$^{-1}$ represented C-H bending vibrations [64]. FTIR spectrum of the NiFe$_2$O$_4$-MWCNTs ($\gamma$=1) composite showed absorptions, which were not observed in a spectrum of the mechanical mixture. Such absorptions were attributed to adsorbed CB. The
absorptions at 1550, 1450 and 1390 cm\(^{-1}\) resulted from aromatic rings stretching \(\nu(\text{C─C})\) and \(\nu(\text{C═C})\) [61]. Small peaks at 1345 and 1325 cm\(^{-1}\) can be attributed to \(\nu(\text{C─N})\) and \(\nu(\text{C═N})\) stretching vibrations [61]. The absorptions at 1255 and 1215 cm\(^{-1}\) represented the \(\text{C─O}\) and \(\text{C═O}\) vibrations, respectively [62]. The absorption at 1175 cm\(^{-1}\) resulted from aryl oxygen stretching [63]. The bands at 1110 and 1072 cm\(^{-1}\) represented C-H bending vibrations [64].

Figure 7.3 FTIR spectrum data for (a) mixture of NiFe\(_2\)O\(_4\) with MWCNTs and (b) NiFe\(_2\)O\(_4\)-MWCNTs composite, prepared using CB, for \(\gamma=1\).

The microstructure of the composite prepared using the CB dispersant is shown in Figure 7.4. The TEM data coupled with the related EDX line scan and mapping data show NiFe\(_2\)O\(_4\) nanoparticles attached to MWCNTs. The TEM images indicate good mixing of the NiFe\(_2\)O\(_4\) nanoparticles and MWCNTs, which is important for the electrochemical performance of the composite.
Electrochemical testing is performed on the electrodes, containing individual materials, their mixture and composites prepared using CB as a dispersant. Previous investigations show that the performance of supercapacitor electrodes decreases significantly with increasing mass loading and highlights the need to develop efficient electrodes with high active mass above 10-20 mg cm\(^{-2}\), which is necessary for practical
applications. Therefore, in this investigation, special attention is focused on the fabrication of electrodes with high active mass, a synergistic effect of NiFe₂O₄ nanoparticles and MWCNTs, and beneficial effect of CB.

Figure 7.5 compares electrochemical testing results for 20 mg cm⁻² NiFe₂O₄ electrodes, 20 mg cm⁻² MWCNTs electrodes and 40 mg cm⁻² electrodes that contain a mechanical mixture of 20 mg cm⁻² NiFe₂O₄ and 20 mg cm⁻² MWCNTs. The CVs for the 20 mg cm⁻² NiFe₂O₄ electrodes and 20 mg cm⁻² MWCNTs electrodes show relatively low currents Figure 7.5 (A) and capacitances Figure 7.5 (B). The highest capacitance of the NiFe₂O₄ electrodes is 0.058 F cm⁻² at a scan rate of 2 mV cm⁻². The capacitance decreases to 0.005 F cm⁻² at a scan rate of 100 mV s⁻¹ due to the poor electronic conductivity of NiFe₂O₄. The capacitance of MWCNTs electrodes is about 0.23 F cm⁻² at 2 mV cm⁻² and it shows very small variations as the scan rate increases, attributed to a double layer capacitance. Electrodes containing the NiFe₂O₄ and MWCNTs mixture show a significantly higher CV area Figure 7.5 (A) and likewise a higher capacitance Figure 7.5 (B), compared to those for the individual materials. The capacitance of the electrode containing NiFe₂O₄ and MWCNTs mixture is 0.89 F cm⁻², which is significantly higher than the sum of the capacitances of the electrodes containing the individual components. Therefore, the result indicates that the two materials have synergistic effects. This enhanced capacitance results from better utilization of the capacitive properties of NiFe₂O₄ in the presence of conductive MWCNTs additives. The results of EIS presented in the Nyquist plot Figure 7.5 (C) show a relatively large real part of the complex impedance, which indicates high resistance. This resistance decreases significantly after the addition of MWCNTs. Therefore, efficient
electron transfer is a critically important factor influencing the capacitive properties of NiFe$_2$O$_4$. The capacitive properties of the electrodes were also analyzed by calculating the real ($C_s'$) and imaginary ($C_s''$) parts of the capacitance derived from the impedance data Figure 7.5 (D,E). The frequency dependence of $C_s'$ and $C_s''$, shows that $C_s'$ for the mixture is significantly higher than the sum of the contributions of the individual components, which is in agreement with CV data. The electrodes, containing the NiFe$_2$O$_4$ and MWCNTs mixture have a relatively high relaxation frequency corresponding to the $C_s''$ maximum, indicating improved capacitive properties over a relatively wide frequency range as compared to pure NiFe$_2$O$_4$ electrodes.

Figure 7.5 (A) CVs at a scan rate of 2 mV s$^{-1}$, (B) $C_s$ versus scan rate, (C) EIS Nyquist plot, (D) $C_s'$ versus frequency and (E) $C_s''$ versus frequency for electrodes, containing (a) 20 mg cm$^{-2}$ NiFe$_2$O$_4$ (b) 20 mg cm$^{-2}$ MWCNTs, and (c) a mixture of 20 mg cm$^{-2}$ NiFe$_2$O$_4$ and 20 mg cm$^{-2}$ MWCNTs.
The capacitive properties of NiFe$_2$O$_4$-MWCNT composites prepared using CB as a dispersant are presented and compared with capacitive data (Figure 7.6) for the mechanical mixtures with $\gamma=1-4$, where the total active mass of the electrodes is 40 mg cm$^{-2}$. Figure 7.6 compares electrochemical testing results for the electrodes with $\gamma=1.5$. The electrodes prepared with CB as a dispersant show a significantly larger CV area, especially in the potential range of -0.4 – 0.0 V. The capacitances for electrodes prepared with and without CB dispersant are 2.17 and 0.84 F cm$^{-2}$, respectively, at a scan rate of 2 mV s$^{-1}$. EIS measurements show relatively low $Z'$, however electrodes prepared with CB show higher $Z'$ despite the higher currents observed in the CV data. The real part of the capacitance $C'$ at low frequencies for the electrode prepared without CB is comparable with the corresponding $C_s$ values at low scan rates. Electrodes prepared using CB have higher capacitances at low frequencies, but $C'$ derived from the EIS data was lower than the $C_s$ obtained from the CV data.

The difference in the EIS and CV capacitances has also been observed in other investigations [65] and attributed to the existence of redox sites with a wide range of redox potentials. Hence, EIS data is obtained at a low voltage of 5mV when some redox sites do not contribute to the capacitance. Both electrodes showed relatively high relaxation frequencies corresponding to the $C_s$" maxima.
Figure 7.6 (A) CVs at scan rate of 5 mV s\(^{-1}\), (B) capacitance versus scan rate, (C) EIS Nyquist plot, (D) \(C_s'\) versus frequency and (E) \(C_s''\) versus frequency for NiFe\(_2\)O\(_4\)-MWCNTs electrodes with \(\gamma = 1.5\), prepared (a) without CB (b) using CB as a dispersant.

Figure 7.7 compares electrochemical measurements for electrodes prepared using CB at different \(\gamma\). The CVs have enlarged areas Figure 7.7 (A) in the -0.4 – 0 V potential range. The capacitances, obtained at a sweep rate of 2 mV s\(^{-1}\), were 2.33, 2.15 and 1.91 F cm\(^{-2}\) for \(\gamma = 1\), \(\gamma = 2.5\) and \(\gamma = 4\), respectively Figure 7.7 (B). Comparing the data shown in Figure 7.5 and Figure 7.7 indicates that electrodes with \(\gamma = 1\) prepared using CB have significantly higher capacitances as compared to electrodes prepared without CB. Electrodes prepared using CB and \(\gamma = 1\) have improved capacitance retention at higher sweep rates and significantly higher capacitances at 100 mV s\(^{-1}\) compared to other electrodes. The lowest electrode resistance occurs at \(\gamma = 1\) Figure 7.7 (C).
The results of impedance spectroscopy agree with the results of CV measurements and reveal that the highest $C_s'$ occurs at $\gamma = 1$. Electrodes prepared using CB show relatively high relaxation frequencies, indicating good capacitive response at high frequencies.

Figure 7.7 (A) CVs at scan rate of 10 mV s$^{-1}$, (B) capacitance versus scan rate, (C) EIS Nyquist plot, (D) $C_s'$ versus frequency and (E) $C_s''$ versus frequency for NiFe$_2$O$_4$ - MWCNTs electrodes prepared using CB for (a) $\gamma = 1$, (b) $\gamma = 2.5$ and (c) $\gamma = 4$.

The charge-discharge behavior of the electrodes is also investigated at different constant current densities in the 3-40 mA cm$^{-2}$ range. Electrodes with $\gamma = 1$ show the largest charge-discharge times, particularly at high current densities Figure 7.8 (A,B). This is attributed to their higher capacitance, which is determined from the discharge data and presented in Figure 7.8 © versus current density. The capacitance for electrodes with $\gamma = 1$ exhibits small
variations with increasing current density, which, in agreement with the CV data, indicates good capacitance retention at high charge-discharge rates Figure 7.7(B). The Coulombic efficiency remains close to 100% after 1000 cycles, however the capacitance retention reduces to 85% Figure 7.8 (D). Therefore, further investigation must focus on the improvement of the cyclic stability of the electrodes.

Figure 7.8 (A) Charge-discharge curves at current densities of 3 mA cm⁻² and (B) 40 mA cm⁻², (C) capacitance versus current density for NiFe₂O₄-MWCNTs composites with (a) \( \gamma = 1 \) (b) \( \gamma = 2.5 \), and (c) \( \gamma = 4 \). (D) (a) Capacitance retention and (b) Coulombic efficiency versus cycle number for \( \gamma = 1 \).

The experimental measurements indicate that the capacitance of the NiFe₂O₄ electrodes is enhanced by adding conductive MWCNTs and using CB as a multifunctional dispersant.
However, the mechanism of capacitance enhancement in composites that are prepared with CB as a dispersant is not well understood. Analysis of the experimental results and available literature allow us to suggest a mechanism. The enhanced dispersion of NiFe$_2$O$_4$ and MWCNTs in the presence of CB indicates that CB is partially adsorbed on the electrode materials. The non-adsorbed CB is washed away during the material preparation. As mentioned above, CB adsorption on NiFe$_2$O$_4$ nanoparticles involves catecholate type bonding Figure 7.1(B), whereas π-π interactions promote CB adsorption on MWCNTs. The isoelectric point of NiFe$_2$O$_4$ is located at pH~6.7 [66]. Application of a negative potential to the electrode usually results in a local pH increase due to electrode reactions in aqueous electrolytes [67, 68]. Therefore, NiFe$_2$O$_4$ particles can be expected to acquire a negative charge and promote electrostatic attraction and adsorption of positively charged CB.

Different mechanisms can enhance the capacitance of electrodes containing adsorbed catecholate molecules. Catechol exhibits redox reactions related to the oxidation of its phenolic OH groups [69]. Catechol-modified carbon cloth electrodes have enhanced capacitance due to the contribution of electrochemical oxidation of the OH groups of catechol [69]. Redox properties of catechol, related to oxidation of their phenolic OH groups, are used for electron transfer mediation in capacitive-type electrochemical biosensors[70]. Several electron transfer mediators are used to develop electrochemical biosensors and enhance their current response significantly. However, the two mechanisms described above and based on catechol oxidation at positive potentials cannot explain the higher capacitance of the CB modified NiFe$_2$O$_4$-MWCNTs electrodes in the negative potential range. In both mechanisms, the OH groups of catechol were not involved in the
adsorption on the electrode material. In contrast, adsorption of catecholates, such as Tiron and Alizarin Red on inorganic surfaces, involves chelating or bridge bonding of their phenolic OH group to metal atoms on inorganic surfaces [71-74]. This bonding facilitates electron transfer from inorganic materials to organic materials [71-74]. A similar adsorption mechanism is involved in CB adsorption on NiO nanoparticles [75]. In contrast to other catecholate molecules, CB also exhibits redox properties in a negative potential range through the following reduction reaction [75]

$$C_{17}H_{18}N_3O_4^+ + 2H^+ + 2e^- \leftrightarrow C_{17}H_{18}(NH)(NH)NO_4^+$$  \hspace{1cm} (Eq. 7.1)

The adsorbed redox-active CB facilitated electron transfer occurs during an electrocatalytic process in the negative potential range [75] above ~ -0.5V. This improvement in the electrochemical response of the electrode results from a charge transfer mediation mechanism [75]. Therefore, it is suggested that catecholate bonding of CB to the Ni or Fe atoms on the NiFe$_2$O$_4$ surface and redox reaction (Eq. 7.1) facilitates electron transfer to electrochemically active NiFe$_2$O$_4$ and enhances the capacitance of the electrode.

The pseudocapacitive properties of NiFe$_2$O$_4$ in the negative potential range are attributed to the reduction of Fe$^{3+}$ to Fe$^{2+}$, which has a lower magnetic moment. However, the magnetic ordering in ferrimagnetic oxides is influenced by the magnetic moments of the paramagnetic ions involved in super-exchange interactions. Therefore, the change in the valence state of the paramagnetic ions and their magnetic moments in the pseudocapacitive redox reactions can potentially result in interesting magneto-pseudocapacitive effects in MOPC. The results of this investigation indicated that enhanced electron transfer is an important factor for the observation of the pseudocapacitive behavior of such materials.
7.5 Conclusions

This study demonstrates how the pseudocapacitive properties of electrodes are advance with ferrimagnetic NiFe$_2$O$_4$ ceramic nanoparticles. A high 2.33 F cm$^{-2}$ capacitance is achieved at low resistance for an active mass of 40 mg cm$^{-2}$ and $\gamma=1$. The electrodes show good capacitance retention with increasing CV scan rate, GCD current density, and EIS frequency. The capacitance decreases with increasing $\gamma$ in the 1-4 range. The high capacitance results from the synergistic effect of NiFe$_2$O$_4$ and the conductive MWCNT additive, and the application of CB as a co-dispersant and electron transfer mediator. The multifunctional properties of CB result from the polyaromatic chemical structure of this molecule that contains a catechol group, its electric charge and redox-active properties. The results open an avenue for fabricating advanced ceramic MOPC materials by combining pseudocapacitive and ferrimagnetic properties.

7.6 Declaration of competing interest

The authors do not have any conflict of interest to report.

7.7 Acknowledgments

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7.8 References


7.9 Supporting informations

Figure 7.9  (A) CVs at scan rate of 5 mV s\(^{-1}\), (B) \(C_s\) and \(C_m\) versus scan rate, (C) EIS Nyquist plot,  (D) \(C_s'\) versus frequency and (E) \(C_s''\) versus frequency for electrodes by 40 mg of NiFe\(_2\)O\(_4\)/MWCNTs for \(\gamma = 1\), prepared by physical mixing and probe sonication of (a) 5 min (b) 10 min.
8.1 Conclusions

Conceptually, new advanced colloidal processing techniques and advanced dispersants from different categories were developed and emerged to synthesis variant well-dispersed composites. Different gamma (γ) ratios (Fe₃O₄ or NiFe₂O₄: MWCNTs) of these synthesized composites have been used in high-performance electrochemical capacitors (ESs) electrodes and devices with high active mass loading and high mass ratio of materials to the current collector. The significant innovations and contributions of this dissertation can be summarized as follows:

- Ultrasonic-assisted chemical synthesis of Fe₃O₄ in situ of activated carbon nanotubes (ACNTs) was efficient to fabricate Fe₃O₄ decorated MWCNTs (M-CNTs). Furthermore, using PA in the bottom-up PELLI method reduced the agglomeration of M-CNTs particles and improved the mixing of the composite components. As a result, well-dispersed M-CNTs composites have been used to fabricate the cathodic supercapacitor electrodes that showed remarkable areal capacitances and low resistance. The highest capacitance of the cathode electrode at high active mass loading of M-CNTs is 5.82 F cm⁻² at 2 mV s⁻¹ that has been achieved for γ=1 and 40 mg cm⁻². For the first time, advanced M-CNTs negative electrodes with a high capacitance comparable to MnO₂-MWCNT positive electrodes at a similar high mass loading have been fabricated, which showed promising performance in a voltage window of 1.6 V.
Celestine blue dye (CB) has been used as a multifunctional dispersing agent in the fabrication of Fe$_3$O$_4$ decorated MWCNTs (M-CNTs) in different ultrasonic-assisted chemical synthesis methods, in situ-chemical precipitation (CCP) and physical mixing (PM). Celestine blue has been proved to promote the coating, dispersion and increase the conductivity of the active material by working as a charge transfer mediator for Fe$_3$O$_4$ and MWCNTs. The M-CNTs electrodes prepared using in situ (CCP) and 15% CB at different $\gamma$ ratios showed lower resistance and higher capacitance and of 6.17 F cm$^{-2}$ that was achieved for $\gamma=1.50$ at 2 mVs$^{-1}$. The asymmetric device based on negative electrode CB/M-CNTs and negative electrode CB/Mn$_3$O$_4$/MWCNTs have been fabricated, which showed promising performance 2.40 F cm$^{-2}$ at 2 mVs$^{-1}$ with a large voltage window of 1.6 V.

Different multifunctional dispersing agents with multiple coating mechanisms such as celestine blue dye (CB), Pyrocatechol violet (PV), azure A chloride (AAZ), and m-cresol purple (CP) have been used at in situ-chemical precipitation (CCP) method to fabricate M-CNTs and M-CNTs/FeOOH composite materials. The presence of the catechol ligand in (CB) and (PV) has a remarkable effect on the dispersion/coating optimization compared to the effect of the electrostatic interactions that only present in (AAZ) and (CP). For the same $\gamma$ and configurations, the CB/M-CNTs/FeOOH electrode showed relatively higher stability (CV profile) compared to that one made by the CB/M-CNTs composite. The Galvanostatic charge-discharge (GCD) behavior of both CB/M-CNTs/FeOOH and CB/M-CNTs electrodes showed high performance > 5 F cm$^{-2}$ and relative stability at different current densities. The asymmetric device
consists of the CB/M-CNTs/FeOOH as a negative electrode and CB/MnO2/MWCNTs as a positive one has been fabricated, which showed promising performance 2.39 F cm\(^{-2}\) at 2 mV s\(^{-1}\) with a wide voltage window of 1.6 V.

- Ferrimagnetic NiFe\(_2\)O\(_4\) ceramic nanoparticles have been developed to advance the pseudocapacitive properties of negative electrodes by using the application of CB as a co-dispersant and electron transfer mediator and the conductive MWCNT additive. The high areal capacitance of 2.33 F cm\(^{-2}\) has been achieved at low resistance for an active mass of 40 mg cm\(^{-2}\) and \(\gamma = 1\). The increased capacitance results from the synergistic effect of NiFe\(_2\)O\(_4\), and the multifunctional properties of CB result from the polyaromatic chemical structure of this molecule that contains a catechol group, its electric charge and redox-active properties. The results open a route for the fabrication of advanced ceramic MOPC materials by combining pseudocapacitive and ferrimagnetic properties.
8.2 Future directions

In this thesis, it has been demonstrated that new advanced ESs composites have been developed and the several problems related to fabrication have been solved. Therefore, it is extremely important to continue the research for the development of new colloidal techniques and advanced composites for ESs application. Based on the research results in this thesis, promising directions will be proposed such as investigation of new dispersants with variant mechanisms and new materials particularly spinel based metal transition oxide as followings:

- To study the advantages of using solid solutions of Zinc ferrite (ZnFe$_2$O$_4$) in the applications of supercapacitor electrodes and devices.
- To develop and fabricate supercapacitor electrodes with a new redox material strontium ferrite (SrFe$_{12}$O$_{19}$) and vanadium oxides (V$_2$O$_5$, V$_2$O$_3$).