



MARMARA UNIVERSITY
INSTITUTE FOR GRADUATE STUDIES
IN PURE AND APPLIED SCIENCES



ANALYZING VARIOUS PARAMETERS ON SUPERCAPACITOR PERFORMANCE

ÖZLEM BUDAK

MASTER THESIS

Department of Chemical Engineering

Thesis Supervisor

Prof. Dr. Atif KOCA

ISTANBUL, 2020



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ABSTRACT

ANALYZING VARIOUS PARAMETERS ON SUPERCAPACITOR PERFORMANCE

Transition metal oxides with enhanced electrochemical performance are points of interest in the fabrication of high efficient electrodes for supercapacitors. Therefore, in this study, our main purpose is to increase the conductivity and the effective surface area of the electrode composed of nickel-cobalt oxide (NCO) which enables to ease the mass diffusion and electron transport. With this aim, the nanosheets of NCO and NCO-reduced graphene oxide (NCO-RGO) hybrids were produced on nickel-foam substrate by a using facile one-step electrodeposition technique which was first performed. The hybrids of NCO-RGO were simultaneously prepared by the electrodeposition and reduction of GO and NCO, leading to a decrease in the total mass of active material on the electrode surface. The NCO-RGO hybrids were further deposited on the nickel-foam without using any binder; thus, it was avoided to decay in conductivity owing to the resistance of binder. After the optimizing of the number of coating layers, the optimization of GO amounts in the electrolyte comprised of equal moles of nickel and cobalt precursors was employed. Finally, NCO-RGO hybrids were fabricated at different nickel and cobalt molar ratios to determine the best performance. Electrochemical measurements confirmed that the specific capacitance and cycling stability of as-obtained electrodes were remarkably enhanced in the presence of RGO in the structure. The NCO-RGO hybrid which was fabricated from the electrolyte solution involving 0.25 mg of GO, exhibited a quite high specific capacitance as well as extraordinary cycling stability compared to NCO. Furthermore, the results indicated that with the increase in nickel content up to a certain rate, the specific capacitance was considerably increased. Out of all the prepared samples, the NCO-RGO hybrids possessed the highest specific capacitance of 1916.5 F/g at 1 A/g with extraordinary retention of 95.6% at a high current density of 10 A/g even after 3000 charge/discharge cycles. Additionally, NCO-RGO hybrids exhibited a high energy density of 53.90 Wh/kg at the power density of 235 W/kg and remained 41.20 Wh/kg at a high power density of 7500 W/kg, implying the attractive rate capability of these materials. As a result of this study, the NCO-RGO nanosheets having remarkable electrochemical performance have a potential as a promising facile and binder-free electrode for supercapacitor applications in the future.

ÖZET

SÜPERKAPASİTÖR PERFORMANSINDA ÇEŞİTLİ PARAMETRELERİN ANALİZİ

Elektrokimyasal özellikleri iyileştirilmiş geçiş metal oksitleri yüksek performanslı elektrot üretimi için önem taşımaktadır. Bu sebeple, bu çalışmada, asıl amacımız nikel-kobalt oksitten (NCO) üretilen elektroların iletkenliğini ve aktif yüzey alanını artırarak kütle ve elektron transferini kolaylaştırmaktır. Bu amaç doğrultusunda, NCO ve NCO-indirgenmiş grafen oksit (NCO-RGO) hibritleri, nikel-köpüğü süstratı üzerine kolay, tek aşamalı ve ilk kez gerçekleştirilen elektrodpozisyon yöntemi kullanılarak elde edilmiştir. NCO-RGO hibritleri, eş zamanlı gerçekleşen elektrodpozisyon ve indirgeme işlemleri sonucu hazırlanmıştır. Elde edilen hibritlerin elektrot yüzeyi üzerindeki kütlesinin RGO etkisi ile azaldığı belirlenmiştir. Ayrıca, NCO-RGO hibritleri nikel- köpüğü üzerine yüklenirken herhangi bir bağlayıcı malzeme kullanılmamıştır. Bu sayede bağlayıcı kaynaklı direnç ortadan kaldırılmış ve iletkenliğin düşmesi engellenmiştir. Kaplama kat sayısının belirlenmesinin ardından, eşit mol sayıda nikel ve kobalt içeren öncüler ile hazırlanmış elektrolit içerisinde GO miktarı optimizasyonu yapılmıştır. Son olarak, NCO-RGO hibritleri, en iyi performansı saptayabilmek adına farklı nikel-kobalt mol oranlarında sentezlenmiştir. Elektrokimyasal ölçümler göstermiştir ki elde edilen elektrotların spesifik kapasitans ve şarj/deşarj çevrim dayanıklılığı yapıdaki RGO varlığı ile kayda değer ölçüde artmıştır. 0.25 mg GO içeren elektrolitten üretilen NCO-RGO hibrit elektrotu NCO elektrot ile kıyaslandığında mükemmel çevrim ömrü yanı sıra oldukça yüksek spesifik kapasitans sergilemiştir. Ek olarak, yapıda belli oranda nikel içeriğinin artışı ile spesifik kapasitansın arttığı belirlenmiştir. Tüm hazırlanan ürünler karşılaştırıldığında, NCO-RGO hibritleri 1 A/g akım yoğunluğunda en yüksek spesifik kapasitans 1916.5 F/g ve 10 A/g gibi yüksek akım yoğunluğunda 3000 şarj/deşarj çevrim sonucu 95.6% kapasite korunumu elde edilmiştir. NCO-RGO hibritleri güç yoğunluğu değeri 235 W/kg da yüksek enerji yoğunluğu olarak 53.90 Wh/kg değeri elde edilmiş ve enerji yoğunluğu değeri, yüksek güç yoğunluğunda (7500 W/kg) 41.20 Wh/kg olarak belirlenmiştir. Bu sonuçlar, bu malzemelerin dayanaklılığının yüksek olduğunu göstermiştir. Sonuç olarak, oldukça iyi elektrokimyasal özelliklere sahip NCO-RGO malzemesi, gelecekte süperkapasitör uygulamalarında kullanılmak üzere kolay ve bağlayıcı içermeyen elektrot yapımı için umut vaat etmektedir.

SYMBOLS

A	: Surface area of electrode (cm ²)
C_s	: Specific capacitance (C/g, F/g)
d	: Thickness of the dielectric separator (mm)
E	: Energy density (Wh/kg)
F	: Faraday constant
I	: Current (A)
n	: Number of moles of electroactive materials
m	: Mass of the deposited active materials (g)
P	: Power density (W/kg)
R_{ct}	: Charge transfer resistance (ohm)
R_s	: Intrinsic impedance (ohm)
Q	: Total charge (coulomb)
Δt	: Discharge time (s)
ΔV	: Applied potential (V)
Z_w	: Ion diffusion impedance (ohm)
ε₀	: Permittivity of free space
ε	: Relative permittivity
θ	: Half of the scattering angle (°)
λ	: Wavelength of the X-ray light

ABBREVIATIONS

AC	: Alternative current
Co	: Cobalt
CV	: Cyclic voltammetry
DI	: Deionized water
EDS	: Energy-dispersive X-ray spectroscopy
EDLCs	: Electrochemical Double Layer Capacitors
EIS	: Electrochemical impedance spectroscopy
GCD	: Galvanostatic charge/discharge
GO	: Graphene oxide
KOH	: Potassium hydroxide
NCO	: Nickel- cobalt oxide
NCO-RGO	: Nickel-cobalt-reduced graphene oxide
Ni	: Nickel
Pt	: Platine
RGO	: Reduced graphene oxide
SCE	: Standard Calomel Electrode
SEM	: Scanning electron microscopy
XRD	: X-ray diffraction
XPS	: X-ray photoelectron spectroscopy

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1. INTRODUCTION

The energy requirement has increased due to the growing enhancement of technology in society as well as the increasing population. Therefore, numerous efforts have been exerted to enhance an eco-friendly, renewable and low-cost alternative energy resources and their storage applications not only to fulfill current and next-generation energy requirements derived from the depletion of fossil fuels but also to overcome the detrimental effects of greenhouse gas emission. In several relevant fields, batteries and supercapacitors are the most attractive and portable devices based on the electrochemical energy conversion [1-3]. However, batteries have some limits on their power density and overall output voltage due to the slow reaction kinetics originated from poor conductivity. In contrast to the batteries, supercapacitors (electrochemical capacitors) have been considered as emerging devices for energy storage applications with remarkable characteristics including high power density, rapid charge/discharge capability, and ultra-long lifetime [4-6]. Supercapacitors are divided into two categories namely electrochemical double-layer capacitors and pseudocapacitors with respect to the charging process. In the pseudocapacitors, transition metal oxides (NiO, MnO₂, Co₃O₄, Fe₃O₄, etc.) and electrically conductive polymers (polyaniline, polypyrroles, and polythiophene, etc.) are generally utilized as an electrode material through reversible Faradic reactions, leading to higher specific capacitances and energy density with respect to the electrochemical double-layer capacitors. On the other hand, for electrochemical double-layer capacitors, carbon-based materials are used for the electrode material which provides the charging via the adsorption/desorption of ions, resulting in higher power density and longer cycle life owing to their nature of extraordinary conductive carbon-based materials [7, 8].

Electrochemical performance of a supercapacitor can be effectively tuned by several factors, particularly electrode material. To date, transition metal oxides have been a point of interest in the literature due to their remarkably high specific capacitance. [4]. Among many transition metal oxides, nickel-cobalt binary metal oxides are one of the most promising option as pseudocapacitive materials as a consequence of their high theoretical specific capacitances, low costs and low environmental impacts reported previous works. The cobalt content in nickel structure contributes to decrease the resistance of the nickel-based electrode which leads improving the electrochemical activity [9]. However, the

transition metal oxides suffer from poor electrical conductivity which causes to decrease the electrochemical performance. Thus, recent researches are focused on to improve the conductivity of these materials by modifying with carbon-based materials such as carbon black, graphene and derivatives, carbon nanotube, etc. for being preferred as an attractive electrode active material in supercapacitors [10].

Graphene oxide, two-dimensional as carbonaceous material, has high crystal structure and electronic properties. Graphene oxide includes different functional surface groups depending on the synthesis method. Furthermore, the graphene oxides can be readily converted into graphene or reduced graphene oxide by diverse reduction processes [11, 12]. Thus, graphene has received enormous attention for the growth on transition metal oxides due to its impressive physical and chemical features such as large surface area, excellent conductivity, structural flexibility, good chemical stability which confirms in a form of unique structure for supercapacitor applications [7, 13, 14].

There are already several techniques in order to synthesize of transition metal oxides as an electrode active material for pseudocapacitors such as solvothermal/hydrothermal, sol-gel, chemical precipitation, and electrochemical deposition [15]. However, in comparison to these techniques, electrochemical deposition is one of the most facile, feasible, rapid, and easy controllable technique for fabrication materials in nanometer-size including metal, metal oxides, and multi-metal alloy coatings [16, 17]. In addition, with the electrodeposition, there is no binder requirement; because active materials are directly grown on a substrate which prevents the decrease in conductivity because of the resistance of binder [18].

In this study, nickel-cobalt binary metal oxides were synthesized on nickel foam by a one-step electrochemical deposition technique without any binders to be used as an electrode for pseudosupercapacitors. Furthermore, the nickel-cobalt binary metal oxides were synthesized in the existence reduced graphene oxide to increase the conductivity which helps to enhancement on the electrochemical performance. For this purpose, the electrochemical performance of all fabricated electrodes was explored by various electrochemical measurement techniques.

1.1. Energy and Energy Sources

Energy is a crucial requirement for economic and social development as well as the growing living standards of humans. Energy needs are continuously increasing which leads to a gradual increase in demand for electrical power. At present, most of the global energy consumption has depended on fossil fuels being nonrenewable but low-cost [19].

Energy in each form is an imperative product and it strictly takes place in lots of areas for the development of humanity. Energy can be characterized into two main headings which are the primary and the secondary energy, represented in Figure 1.1. The first of these particularly comprises the energy sources with or without separation from the other materials, cleaning or grading, before converting the energy into heat or mechanical work. In other words, all energy forms which are not processed can be counted in the class of primary energy such as crude oil, biomass, and solar, etc. However, secondary energy involves the transformation of the former applying energy conversion methods.

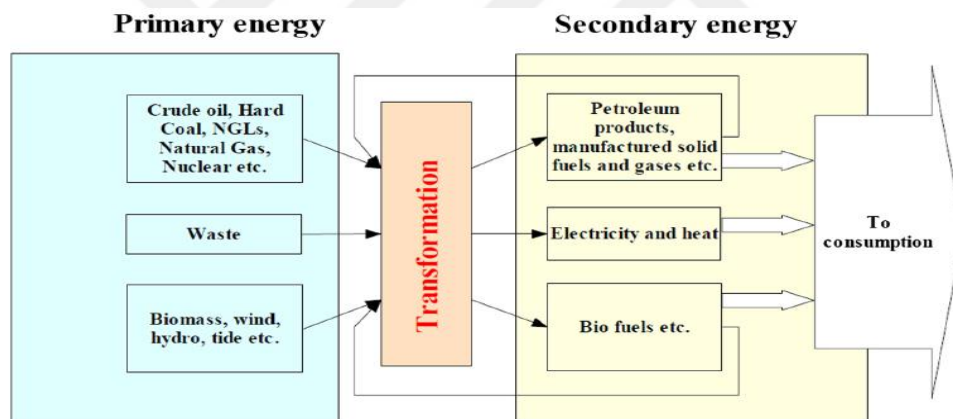


Figure 1.1. Energy forms in primary and secondary [20].

Secondary energy types known as energy carriers can directly be utilized for requirements of society without any conversion processes; hence, it is a more appropriate form of energy. Electricity, diesel, gasoline-ethanol, hydrogen, and heat are some of the types of secondary energy [20].

However, growing energy demand causes to arise recent concerns on the increase of emissions due to greenhouse gases in the environment derived from fossil fuel consumption, resulting in climate change. Besides the harmful carbon emissions, the depletion of fossil fuels is another important issue. Therefore, renewable energy resources such as solar, wind, hydrothermal, biomass, geothermal, wave or tidal have been

attracting considerable interest to efficiently supply the increasing energy demand. [21]. As a result, renewable energy resources with advantages like earth-abundant and eco-friendly is regarded as the most feasible solution for the sustainable energy future by many governments [22].

1.2. Energy Storage

Energy is an important necessity for social and economic development of the humanity. Since the Industrial Revolution, the energy need has corresponded with the combustion of fossil sources. The deficiency and unsteady distribution of the natural resources has already induced several economic issues which provide benefit to reveal various energy generation and storage systems [23]. Furthermore, increasing the exhaustion of fossil fuels, primarily consumed in several forms of energy and detrimental effects of emissions due to the greenhouse gas on the environment leads to arise a huge demand for energy storage applications [24]. Therefore, energy storage applications have gradually become significant in the improvement of the economy and society. In case of the inaccessibility of generated energy for a long utilization, storage has gradually become important. Energy storage technologies collect the energy from different sources and converting them to energy forms required in various areas. It controls the utilization of energy resulting in an increase in energy consumption efficiency.

Fossil fuels can be employed to supply energy depending on the demand; therefore, they can be effortlessly stored when not required. On the other hand, other sources such as solar and wind energy as a renewable energy sources need to be harvested owing to their unsteady nature and must be stored until needed. In other words, despite being eco-friendly, renewable energy resources have been limited by local weather and climate conditions. Such characteristics of renewable energy can give rise to fluctuation in the related utilization areas [22]. Thus, energy storage possesses many advantages to benefit from renewable energy sources, economically. Firstly, the storage of heat and electricity as a secondary energy forms helps to decrease the inadequate primary energy forms like fossil fuels and to accommodate the increase in renewable energy generation. Secondly, energy storage also helps to reduce the greenhouse gas emissions which contribute the global warming. Additionally, the energy storage is considered a vital issue due to its contribution to the energy management. The energy storage application enables not only

to decrease the energy wastage but also to increase the effectiveness of energy consumption. The storage of heat or electricity as a secondary energy form helps to decrease the amount of fossil fuels (primary energy forms) utilization to create them. The energy storage can conduce to planning, operation, and frequency regulation of power plans. It can also facilitate to control the energy system stability and develop the power aspect [25].

1.3. Types of Energy Storage

Energy storage applications can be divided into several groups based on their conversion mechanism as input and output energy forms are considered. Thus, there are two input energy forms namely electricity and thermal energy. On the other hand, besides these, output energy forms have more variety like gaseous and liquid fuels, and other chemicals [26]. Energy storage technologies have been used for years and gone through continual enhancement to improve their performance; although many of them have become mature.

There are many types of energy storage methods can be categorized into two headings which are electrical energy storage and thermal energy storage, presented in Figure 1.2 [20, 27].

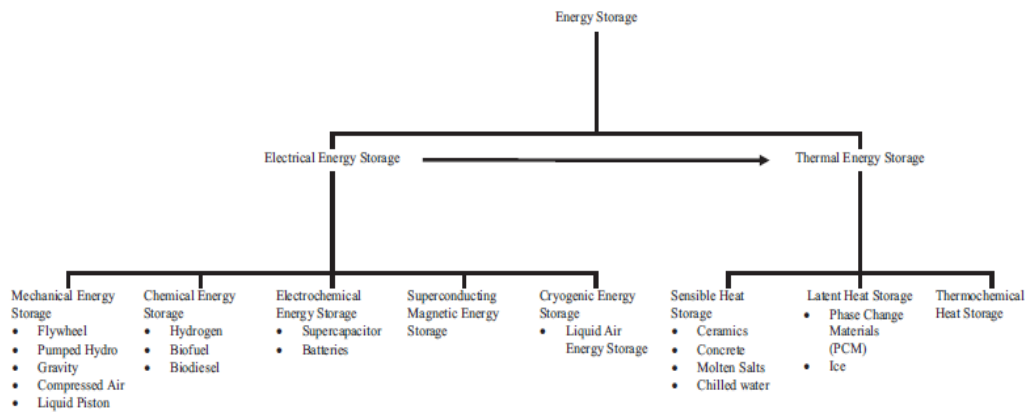


Figure 1.2. Energy storage categorization.

1.3.1. Electrical energy storage

Electrical energy storage approaches are regarded as a highly important point in the progress of sustainable energy technologies. This type of energy storage can also be explained that a process is the converting electrical energy from a power network into a storable form. Thus, it can be converted to back in electrical energy in case of

requirement. The electrical energy storage is a highly efficient process because it can produce the electricity at situations like low demand, low cost from irregular renewable energy and can enable to utilize it at high demand, high cost or as an alternative in case there is no other generation access. Besides being efficient, the electrical energy storage has a great variety of utilization fields involving portable devices, transport machines, and stationary energy sources [28].

There are different technologies considered as electrical energy storage technologies which use to convert electricity into other forms of energy that can easily be stored. Such technologies can be known as mechanical energy storage, chemical energy storage, electrochemical, superconducting magnetic energy storage.

1.3.1.1. Electrochemical energy storage

The extensive global utilization of fossil fuels has led to the accumulation of carbon in the natural cycle, resulting in the greenhouse emissions. CO₂ known as the main greenhouse gas has detrimental effects on environmental; hence, renewable energy sources such as solar, wind, geothermal, waves, and electrochemical energy have become a significant energy source type to meet the energy requirement of humanity. Therefore, over 18% of the worldwide energy consumption presently originates from the renewable energy sources because of their long-term availability, approachability, and eco-friendly [29]. Among the other types of renewable energy, electrochemical energy with the numerous advantages is a promising option for the future applications. The electrochemical energy storage mechanism is based on converting chemical energy to electrical energy with electron and ion transportation.

In the late 18th century, electrochemistry and energy conversion have gained importance. Galvani's experiments indicated that living systems both are affected by electricity and produce it. The beginning of modern battery applications is considered as the development of Volta's pile which consists of zinc and silver separated by a cloth or paper. Later, Nicholson and Carlisle employed to the pile in order to electrolyze water, encouraging many scientists containing Berzelius, Davy, Faraday, Kohlrausch, and others. Kohlrausch, and others. In 1839, besides batteries and electrolyzers, fuel cells as a novel electrochemical energy conversion device explored by Grove. In the early 1900s, there were impressive advances in lead-acid batteries, resulting to increase their

application in many related fields such as cars, notebooks, and communication/entertainment tools. Finally, electrochemical energy conversion has been remarkably progressed in the late 1960s and early 1970s in case of confirmation of water splitting by using a semiconductor electrode [30].

Batteries, capacitors and supercapacitors are the common energy storage devices that perform depend on the electrochemical energy conversion mechanism. These devices have solid substances with specified chemical formulation and morphology called electrode where the electrons and ions store [31].

Specific energy/power density, lifespan, rate capability, and safety are critical parameters for energy storage systems [32]. Specific energy density is calculated by dividing the accumulated energy to volume or mass, and specific density is the ratio of the energy transfer rate to volume or mass [27]. Batteries, in particular lithium-ion batteries, are mostly preferred owing to their high energy density and long life cycle performance [32]. However, batteries have comparably low power density and high internal resistance, which could diminish their power-delivery capability in case of large current applications. Supercapacitors with relatively high power density, high specific capacitance, rapid charge/discharge capability, and enhanced long cycle life have gradually drawn much attention than batteries for energy storage [33]. Beyond the low energy density, supercapacitors can help to solve various energy problems of rural areas where there is not an accessible communal grid. Supercapacitors also can be used as power supplies for portable devices like mobile phones, digital cameras, notebook computers, etc [23, 33].

The performance of electrochemical energy storage approaches in terms of energy/power density generally stands for Ragone Plot (Figure 1.3) which guides to distinguish the convenient storage type for applications according to energy storage capacities [27]. In accordance with the Ragone plot, batteries own high specific energy and low specific power. On the other hand, supercapacitors where involve the territory between conventional capacitors and batteries, possess exceedingly high power density, whereas they have limits for operations demanding high specific energy [34, 35]. However, creating the Ragone plot, many other performance criteria like safety, repetitive lifespan, and cost are not evaluated. Therefore, it needs to be noticed that when a particular energy storage system is selected, all parameters must be taken into consideration [36].

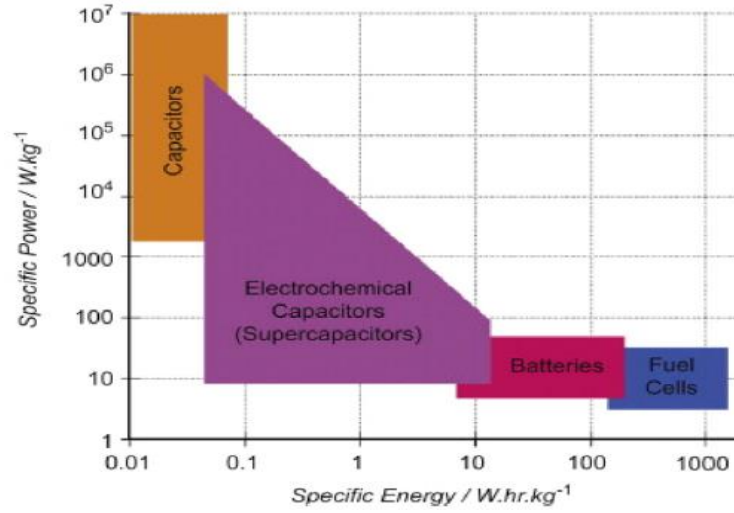


Figure 1.3. Ragone plot for energy storage [27].

1.3.1.2. Electrochemical energy storage mechanism

Such systems can be capable of chemical and electrical energy conversion indirectly and reversibly. Chemical energy is principally accumulated in the chemical bonds. With the electrochemical reactions, active electrode materials which have high bond energy are turned into the substances with low bond energy resulting in generation of electrical energy. Electrodes can be prepared by using various materials with different electrochemical potentials. Materials with high electrochemical potential are formed during the storage of electrical energy in the electrodes. Subsequently, when the substances having high electrochemical potential convert to low ones, chemical energy is simultaneously formed [37].

The change of total Gibbs free-energy derived from the electrochemical reactions depends on the electrode material. When the charges are transferred, the occurred theoretical cell voltage is determined by the subsequent equation: [38]

$$\Delta E = -\Delta G / (n \times F) \quad (1.1)$$

The energy difference of a given chemical reaction occurring due to the charge and discharge can be expressed with the help of the following formulation. The change in Gibbs free energy ΔG obtained from the chemical reaction due to the charging/discharging is calculated through the subsequent equation [31]:

$$\Delta G = \Delta U + P\Delta V + V\Delta P - T\Delta S - S\Delta T \quad (1.2)$$

where U states internal energy, P, T, and V represent pressure, temperature and volume, respectively. When the operation conditions (pressure, volume, and temperature) are constant and there is only an electrical work, the Nernst equation becomes [31]:

$$\Delta G = -z \times F \times V \quad (1.3)$$

Z is calculated by dividing the amount of transferred electrons to the mole, F is Faradaic constant, and V denotes the performed voltage.

1.4. Applications to Electrochemical Energy Storage

1.4.1. Batteries

A battery is a kind of transducer that produces electrons via electrochemical reactions and consists of an anode, a cathode, a separator, and a supporting solution. The materials principally used for the cathode supported onto an aluminum current collector are oxide of lithium manganese, lithium cobalt oxide, and lithium nickel cobalt manganese oxide, etc. and the materials used for the anode supported on to a copper current collector are metallic lithium, lithiated carbon, graphitic carbon, synthetic graphite, and tin-based alloys, etc. LiPF₆, LiClO₄, LiAsF₆, and LiCF₃SO₃ are preferred as a supporting solution called electrolyte [39]. The mechanism of a battery is essentially based on reduction and oxidation (redox) reactions. In this mechanism, energy is stored during charging and subsequently, it is utilized to accomplish the process during discharging. Once the battery is being discharged, the oxidation/reduction reaction occur at the anode and cathode, respectively. The electrolyte is imperative for these reactions to arise owing to that it provides the transportation of positive ions between the electrodes. With the ion transportation, charges which form during the redox reactions at each electrode, neutralize and thus the continuity of the chemical reactions is properly ensured [40]. The anode and cathode electrodes are split with the help of a separator which is comprised of a porous membrane such as glass fiber, cellulose, inorganic composite membranes, and microporous polymer membranes. The membrane permits the ions transition but prevents interaction of the electrodes with each other's. When a charge connects to a battery, electrons change place from the negative electrode to the positive electrode which creates an electrical energy [41]. An illustration summarized the charge/discharge process of batteries is given in Figure 1.4.

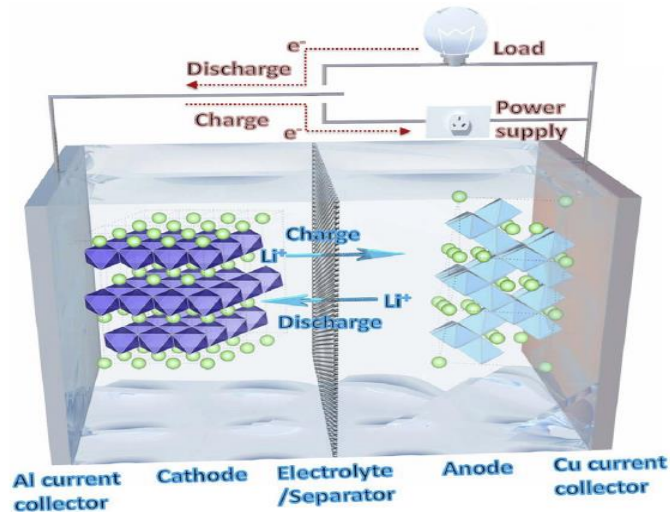


Figure 1.4. The illustration of a conventional lithium-ion battery and its electrochemical charge/discharge system [41].

The potential of the battery is estimated from the difference between the chemical potential of the lithium in the anode and cathode. Generally, a battery involves one or more cells that provides the conversion of the chemical energy into the electrical energy form [39]. The theoretical capacitance of a battery can be calculated based on electrochemical reactions involved for both anode and cathode parts. The equation of the theoretical capacity in mAh/g is [38]:

$$C = (2F) / (n \times M) \quad (1.4)$$

where x states the amount of transferred electrons, F is Faraday's parameter, n and M represent the total moles of electroactive materials and molecular weight of the same electroactive material, respectively.

Long lifespan, safety, energy density/capacity, cost, and voltage per cell are critical factors for battery design. Although batteries possess high energy density, they have limitations on cycle stability due to the chemical depletion at active materials during repetitive charge and discharge processes. There are commonly four types of battery: lead-acid, nickel-metal hydride, sodium-nickel-chloride, and lithium-ion batteries to be used for electric vehicles and various energy storage systems [42]. Among the other battery types, lithium-ion batteries is the most principally preferred option for the new energy vehicles especially portable electronic tools like cell phones and laptop computers

because of its high energy density, low discharge rate, good lifetime, etc., in the past few decades [38, 43].

1.4.2. Capacitors

The charge/discharge mechanism of a capacitor differently from the batteries does not involve any energy conversion processes which are derived from the redox reactions, only electrical energy needed to be involved. Therefore, they are also referred to as dielectric capacitors. In the dielectric capacitors, electrostatic energy is stored in the form of electric charges at two or more electrically conductive plates, which are separated by a dielectric material, as presented in Figure 1.5 [44].

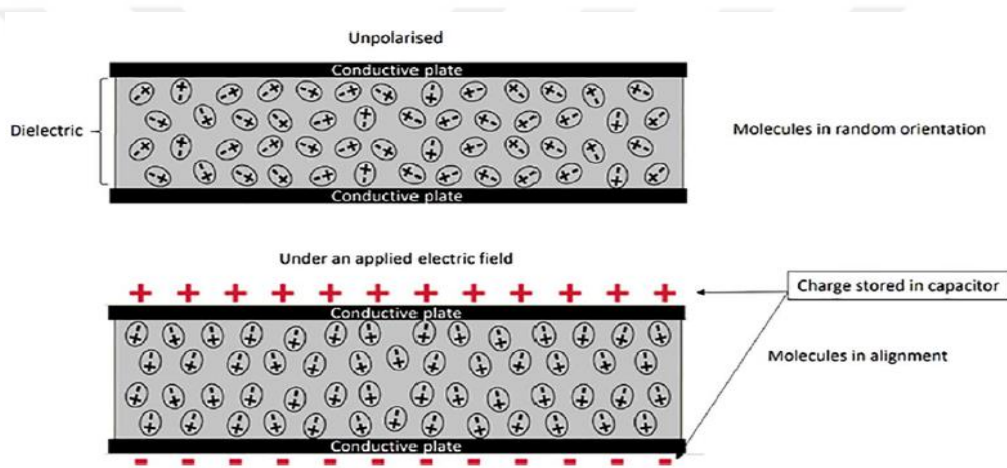


Figure 1.5. A typical illustration of a dielectric capacitor [44].

Conductive plates in parallel positions are fabricated by using various metals. The applying voltage of the capacitor depends on the physical strength of the dielectric material. The area between two conductive plates is quite an important parameter on the performance of dielectric capacitors. Capacitors have a high specific capacitance due to the dielectric polarization which is generated from the inserted dielectric separator between two conductive plates [44].

The storage mechanism of capacitors depends on Coulomb's Law. The capacitance of the dielectric capacitor is determined by the ratio of the entire charge in each plates to the potential difference between the conductive plates [45]:

$$C = Q / V \quad (1.5)$$

in which C is the capacitance in Farads, Q is the total charge in coulombs, and V is the operating voltage between the plates.

Furthermore, the specific capacity of capacitors can be estimated by the following equation [46]:

$$C = (\epsilon_0 \times \epsilon \times A) / d \quad (1.6)$$

where ϵ_0 is the permittivity of free space, ϵ states the relative permittivity, A depicts the area of the capacitor, and d denotes the thickness of the dielectric separator amongst the conductive plates.

The cycle stability of dielectric capacitors is higher as compared to the batteries since there is no any redox reactions during charge/discharge. Besides, the capacitors can charge the electrical energy in a long period and discharge within a short time. But, the specific energy of the dielectric capacitor is lower than the batteries [44].

Capacitors possess high power capacity; therefore, they can be preferred for electric vehicles, hybrid vehicles, electric drive-trains, aircraft powertrains, and shipboard power systems which need high power for acceleration [46].

1.4.3. Supercapacitors

With the continuous growing human population and technology improvement, consumption of energy increases exceedingly, resulting in the deficiency of non-renewable energy resources and environmental issues derived from the greenhouse effects. Therefore, to extinguish these crucial limitations at future applications, environmentally friendly, profitable, and renewable energy sources have become the main subject of much research. Several types of technologies based on renewable energy sources like solar, wind, biofuel, water flow, batteries, fuel cells, traditional capacitors and supercapacitors have been broadly employed in social life and industry to encounter the requirement of energy. Apart from those of devices, supercapacitors, also named electrochemical capacitors are a promising option due to their attractive electrochemical performance like high power density, high stability after numerous of charge/discharge cycle and fast charge/discharge rate capability [47, 48].

First studies about supercapacitors were carried out by US companies General Electric (GE) and Standard Oil of Ohio (SOHIO) in the middle of the 20th century. These supercapacitors patented in 1971 by SOHIO, possessed approximately 1 F capacity. In 1982, Panasonic launched the first commercial supercapacitor called Gold Cap in the marketplace. Then, the first electric double-layer capacitor (EDLC) which is a supercapacitor type, was fabricated for applications of the military by the Pinnacle Research Institute (PRI). In 1992, numerous EDLC type supercapacitors with 1000 F capacity named BoostCap was released to the commercial market by the Maxwell Laboratories. The development of supercapacitors have increasingly proceeded since 2007. These novel supercapacitors have exhibit higher performance as compared to the traditional ones. Supercapacitors used nowadays have reached capacity over many thousands of Farads and also have employed at high current densities for a long time [49].

Supercapacitors serve as a bridge between the conventional capacitors with high specific power and batteries possessed high energy density. However, traditional capacitors are not appropriate to fulfill the future applications because of their rigid and massive structure. As a result, supercapacitors with enhanced properties such as thinness, lightless, and flexibility have many advantages for multifunctional areas [33].

The major difference between the supercapacitors and conventional capacitors is that there is no dielectric material. The typical capacitors involve two or more dielectric plates for electrostatic charge storage. However, supercapacitors comprise of submerged electrodes within a suitable electrolyte medium insulated with the help of a separator which prospers the ions transportation but provides to avoid the contact of electrodes [50]. The performance of supercapacitors on energy storage can be evaluated from the point of electrochemical characteristics detected through interactions amidst the electrode material and the electrolyte solution [23].

Supercapacitors involve electrodes with a greater effective surface area which induce higher specific capacitance and higher power density compared to conventional capacitors and batteries. Furthermore, the operating temperature range is a sufficient parameter to consider for estimating the chemical performance of energy storage appliances. Supercapacitors can perform in a very wide temperature range between -40°C to 100°C superior to the batteries [23].

1.5. Supercapacitor Applications

Supercapacitors are principally utilized in areas, in which is an urgent requirement to store or delivery a large amount of energy in a very short period. Thus, they are mostly applied in hybrid electric/electric machines, and fuel cell machines such as cars, trains and some kind of buses, cranes, and elevators at present. Supercapacitors can be also used in electronic tools as continuous power equipments and volatile memory spare parts in the computers, mobile phones and, radio tuners [51]. With the unique contribution of supercapacitors in the automotive industry, several benefits have been gained. The hybrid vehicles stop the engine incomplete in the case the car stops. Hence, in the presence of a supercapacitor which can charge in just a few minutes, the car can be capable of a quite powerful start. Supercapacitors can further be utilized in combination with conventional batteries in electric vehicles, leading to the development of performance [49]. Additionally, supercapacitors perform to tune the power efficiency of energy collecting systems, solar arrays, and wind turbines. Supercapacitors supply the stability of power density and play a key role to enhance the power quality of these systems. Supercapacitors also reduce the occupied stress on the batteries during high current density charge/discharge processes which provide the incensement of the battery lifespan [52].

1.6. Supercapacitors Types

Supercapacitors have been already categorized into three major types according to the storage mechanism, namely electrochemical double-layer capacitors (EDLC), pseudocapacitors, and hybrid supercapacitors composed of their combination [53].

1.6.1. Electrochemical double-layer capacitors

The electric double-layer capacitor (EDLCs) is preferred in many areas, especially digital communication tools and electric vehicles owing to its effective high-power energy storage capability. EDLCs comprise of two electrodes immersed in a suitable electrolyte which split by a separator. EDLC type of supercapacitor also has a double layer at the interface between electrode and electrolyte in which electrical charges are accumulated on the electrode surfaces and oppositely charged ions line up in the electrolyte side. Therefore, EDLCs electrode materials are needed to have a large surface area for

exhibiting higher capacity and have a convenient morphology for fast ion transportation [35].

In EDLCs, the charge storage process derives principally from the separation of ions at the interface of electrode and the electrolyte medium [54]. In other words, the capacitance mechanism of EDLCs essentially resembles the capacitance mechanism of a conventional dielectric capacitor. However, EDLCs having a large surface area electrode can be competent to store much more energy as compared to traditional capacitors. The energy storage of this type of capacitors is depended on the electrostatic mechanism because of the incorporation of ions of electrolyte on the active material surface. The capacitance of EDLCs is generated as a result of charge separation taking place because of the polarization at the interface between the electrode and electrolyte. The charge accumulation arises from straightly across the double layer in the absent of charge transportation through the interface. Thereby, the capacitance occurs because of the real capacitance effect. The surface charge creation process rises in the nature of the disseverance of the surface, adsorption of ions from electrolyte, and deformity in the pore structure of active electrode material. The inadequacy or excess of charge generation on the electrode surface causes the formation of ions of opposite charge belong to the electrolyte solution adjacent to the interface of electrode/electrolyte for providing electro-neutrality [50].

Double-layer capacitance composed of the separation of opposite charge at the interface of electrode and electrolyte was introduced in the 19th century by Helmholtz. In accordance with the Helmholtz model represented in Figure 1.6a, separated charges are arranged at between the electrode and electrolyte interface in order of a tiny gap. Gouy and Chapman have revised the model into the diffusive layer model (Figure 1.6b). In the diffusive layer model, the achieved capacitance of two separated layers depends on their distance. The concept of EDLCs is commonly similar to the conventional dielectric capacitors. Hence, with the presence of point charges near to the active material surface, higher capacitance could be acquired. An integrated model formed of the mentioned models was proposed by Stern. As schematically shown in Figure 1.6c, this model involves an inner region between two regions, named Stern layer.

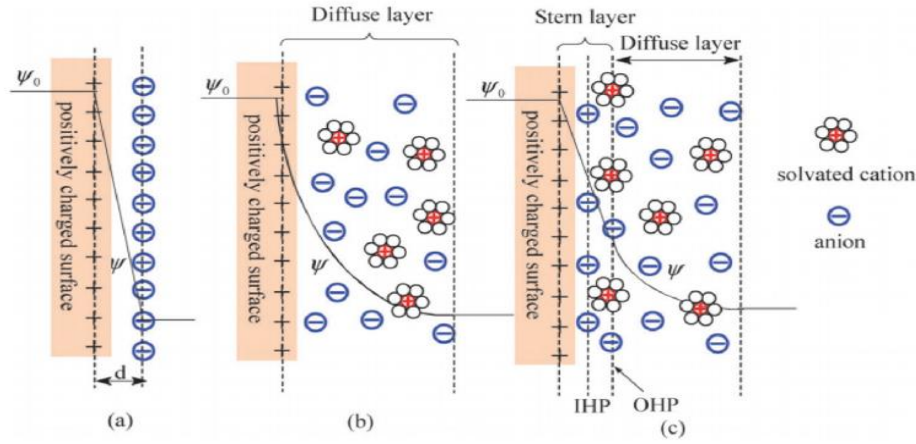


Figure 1.6. (a) the Helmholtz model; (b) the Gouy–Chapman model; (c) the Stern model [23].

Ions behave as an impressive adsorbate for the conductive material with the addition of the Stern layer. The Stern layer further encloses specific adsorbate ions and nonspecific adsorbate (opposite) ions which are divided into the inner and outer Helmholtz planes. The energy due to the motion of opposite ions leads to the diffusive layer region of the model. The capacitance of an EDLC is equal to the sum of Stern layer capacitance and the diffusive region capacitance. The EDLCs electrode has a high specific area due to the high porosity which directly correlated with the charge storage. Therefore, the ions transportation process is mainly controlled by the affinity of mass transfer way, the achieved area remained from the pores and the wettability by the solution.

The specific capacitance for EDLCs can be determined from the following equation [50]:

$$C = (\epsilon_0 \times \epsilon_r \times A)/d \quad (1.7)$$

in which ϵ_r is the dielectric constant of the basic solution, ϵ_0 stands for vacuum permittivity, A is a specific surface area, and d represents thickness of the double-layer.

1.6.1.1. Electrode materials for EDLCs

The charge storage of EDLCs depends upon the reversible adsorption of ions of the electrolyte onto electrode materials. Therefore, various carbonous materials like activated carbon, carbon aerogels, carbon nanotubes, carbon nanofibers and especially graphene, and graphene derivatives, having large surface area as a result of its attractive porous structure are used for the active electrode material. Furthermore, carbon-based materials

not only exhibit exclusive electrical, chemical and mechanical stability but also have relatively low cost, non-toxicity, and easy processability; hence they evolve into an indispensable option for the application of EDLCs [7, 12].

1.6.1.2. Introduction to Graphene Oxide

Graphite is a kind of natural mineral having a very anisotropic structure that exhibits remarkably good electrical, mechanical, and thermal characteristics. Therefore, the graphite is widely utilized for various applications, especially the production of strong oxidizing agents named as graphene oxide (GO) [12].

GO is the monolayer structure of graphite oxide, having sp^2 hybridized carbon atoms in a honeycomb crystal lattice. The graphene oxide is easily produced from the flake graphite and possesses such a layered structure, being dispersible in water. The graphene oxide includes various surface oxygen-involving chemical sites like hydroxyl carboxyl and epoxy depending on the production procedure (Figure 1.7). These carboxylic groups at the edges of the structure allow the good dispersion of GO in the form of a single sheet. Thus, GO with good dispersion ability is a promising material for several areas in particular synthesis graphene-based materials [55].

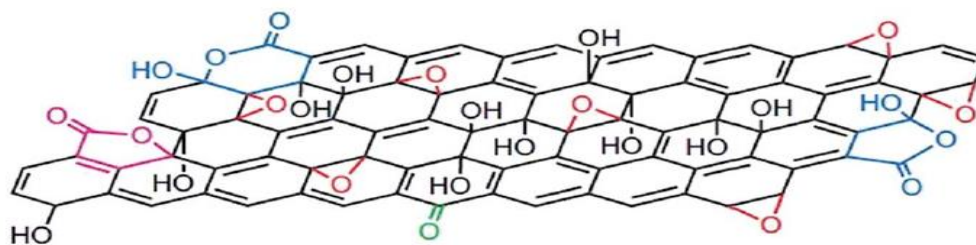


Figure 1.7. The structure of GO [56].

GO exhibits remarkable features like a high specific surface area, superior mechanical durability, tunable electrical, and optical properties and high interaction with other materials due to its functional groups. Thus, GO with enhanced texture diversity and improved properties has been attracted in versatile applications such as energy storage areas as an electrode material, photocatalyst for water splitting process, removal of air pollutants and water purification, [57].

1.6.1.3. The background of the graphene oxide synthesis methods

B.C. Brodie developed the production of graphene oxide in 1859 by mixing some of the KClO_3 to a blend of flake graphite and concentrated fuming HNO_3 . Brodie was able to be successful in increasing the oxygen content in the structure through the several oxidative treatments. In 1898, L. Staudenmaier modified the procedure by adding multiple aliquots of KClO_3 in the mixture and using concentrated H_2SO_4 as well as HNO_3 to increase the acidity of the mixture. Thus, he synthesized a graphene oxide in the form of highly oxidized in a single reactor, leading a more practical process for graphene oxide production [56]. In 1958, an alternative procedure for the production of GO was reported by Hummers and Offeman which is most widely used today. In mentioned procedure, the oxidation of graphite is carried out by the mixture of KMnO_4 and NaNO_3 in concentrated H_2SO_4 . Recently, Marcano et al. enhanced a novel procedure for the production of graphene oxide by excluding sodium nitrate and increasing potassium permanganate, named “Improved Method”. In this procedure, the efficiency of graphene oxide synthesis is much higher among the other methods; in other words, it provides a greater amount of graphene oxide. In addition, this procedure is superior to generating any toxic gases during the process such as NO_2 and N_2O_4 [55].

1.6.1.4. Reduction of graphene oxide

The well-known reaction of GO is a reduction in reduced graphene oxide (RGO) by removing the functional groups. In general, RGO layers are virtually regarded as chemically derived graphene shown in Figure 1.8. The destruction due to the sp^2 carbon bonding network derived from functional groups makes the graphene oxide electrically insulating; hence, the conversion of GO becomes the main issue to produce a much less defective form. With the reduction of GO, the p-network structure is re-arranged which contributes to increase the conductivity of resulting RGO sheets [58].

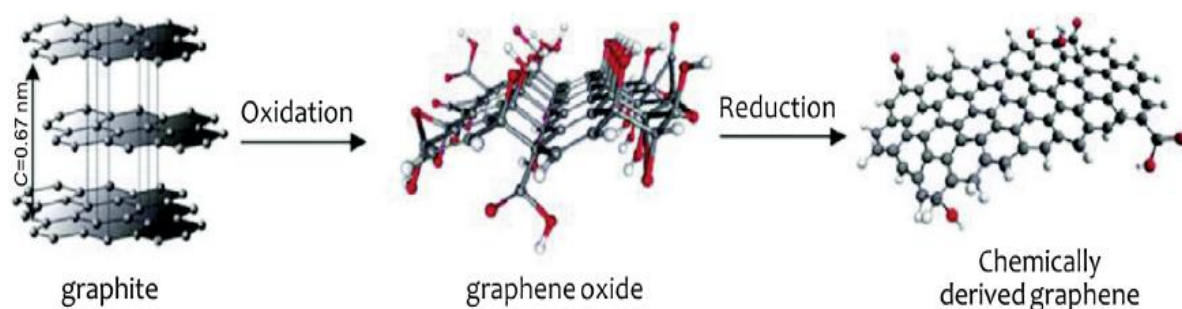


Figure 1.8. The conversion of the graphite into the chemically derived graphene [12].

1.6.1.5. Reduction strategies

Several methods are available in order to convert GO into RGO and the important ones are listed in the following sections.

1.6.1.5.1. Thermal reduction

RGO can be generated by heat treatment which is designated as thermal reduction. In this process, rapid heating is employed to exfoliate graphite oxide to produce RGO. During rapid heating, an abrupt expansion due to the rising of CO or CO₂ gases is grown into the space amidst graphene layers. As the temperature increases, the oxygen-involving sites located on the carbon plane degrade to gases, resulting in great pressure between the stacked sheets. With the thermal treatment, the functional groups are eliminated from the structure; thus, the exfoliated sheets can be called RGO. Furthermore, the annealing atmosphere is another critical parameter for this type of process due to the increment of oxygen at high temperatures. Therefore, the annealing process is generally performed in a vacuum, inert or reducing atmosphere. However, thermal reduction of graphene oxide has some limits such as production just small size and wrinkled graphene layers because of the removing carbon atoms by the decomposition of functional groups. In thermal reduction, some of destructions can also arise in the structure of reduced graphene sheets derived from the release of CO₂ [59].

1.6.1.5.2. Chemical reduction

The mechanism of RGO production by chemical reduction is depend on the reactions between chemical reagents and GO. The chemical reduction process is generally performed at room temperature. Therefore, the need for equipment and atmosphere is not

as critical as that of the thermal reduction process, making the chemical reduction more low-cost and readily applicable method for the generation of RGO than thermal reduction. In the chemical reduction process of GO, the first and most widely chemical reagent was employed as hydrazine (N_2H_4) reported by Stankovich et al. (Figure 1.9). Apart from the hydrazine, there are several typical reducing agents such as alcohol, NaOH/KOH , NaBH_4 , HI , CH_3COOH , and AlH_3/FeH [60].

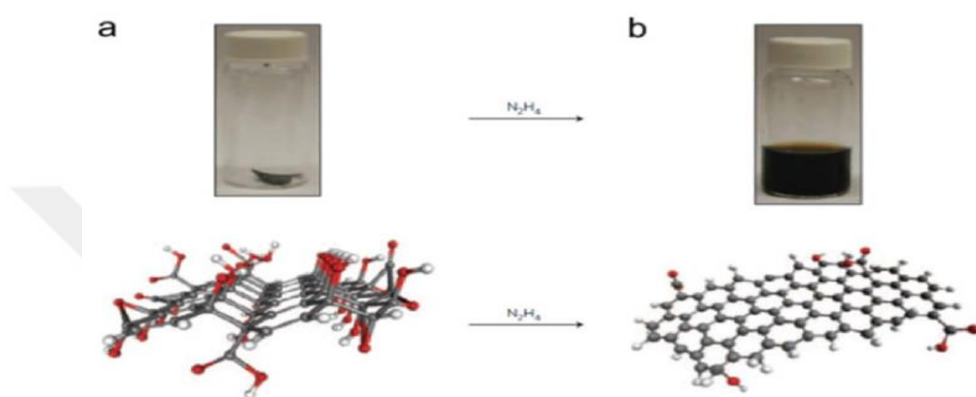


Figure 1.9. An illustrative description of chemically converted RGO suspensions [94]

1.6.1.5.3. Electrochemical reduction

Electrochemical reduction is another attractive method for the reduction of GO into RGO. This process needs no chemical agents, resulting from the removal of hazardous chemicals and the elimination of by-products. The mechanism of graphene oxide is principally dependent on the electron exchange between graphene oxide and electrodes. Such process can be carried out by applying cyclic voltammetry, linear sweep voltammetry, or chronoamperometry in a traditional three-electrode system at ambient conditions. There are two distinct procedures namely one-step and two-step electrochemical reduction, represented in Figure 1.10. In the one-step method, the GO is directly electrochemically reduced from an aqueous dispersed solution to generate the RGO thin sheets on a substrate surface served as an electrode. For the two-step electrochemical reduction, the first stage is the deposition of graphene oxide on a substrate surface, and then there is a drying treatment to generate a GO-deposited electrode. The second stage is an electrochemical reduction by using a suitable electrolyte to provide ERGO layers on the substrate [61].

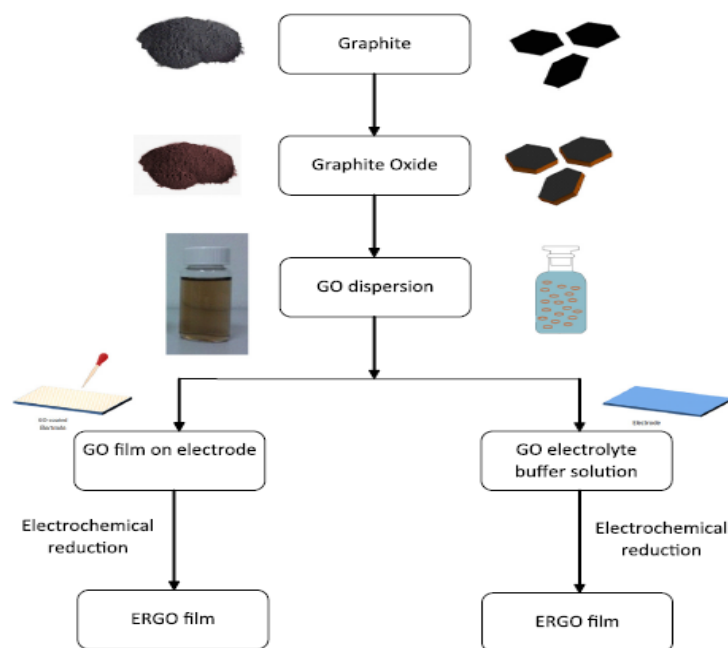


Figure 1.10. Representation of electrochemical reduction process of GO [61].

1.6.2. Pseudocapacitors

The other type of supercapacitors is named pseudocapacitors. In pseudocapacitors, the capacitance occurs in the appropriate electrode material with the execution of potential which leads to a Faradic current occurring from the reactions like as electro-sorption or oxidation/reduction of the electroactive materials. Electro-sorption which is one of these reactions arises when chemisorption of electron-donating anion like Cl^- , B^- , or I^- appears in a mechanism following $\text{M} + \text{A}^- \leftrightarrow \text{MA}^{(1-\delta)-} + \delta\text{e}^-$. In this type of reaction, anions of A^- at the surface of the electrode and the amounts of δe^- directly affect the electro-sorption valence. In contrast to that, the redox reactions succeed as a result of a charge transfer against the double layer instead of the charge separation, represented as $\text{O}_{\text{ad}} + n\text{e}^- \rightarrow \text{R}_{\text{ed}}$. In this type of process, the energy is stored indirectly when the charge magnitude of $n\text{e}^-$ exchanges during the reaction [62].

Apart from the EDLCs, the storage mechanism of pseudocapacitors is related to the oxidation-reduction reactions occurred on the surface of pseudo-electrode. Pseudocapacitor is similar to a battery due to the storage mechanism based on redox reactions. The charge storage is carried out at the electrode surface owing to the charge shift of reversible redox reactions in Faradic nature; hence the term is named as pseudocapacitance [63].

The word of pseudocapacitance refers to a capacitive material of electrochemical nature that is linearly associated with the charge stored on the extent of the voltage range.

The pseudocapacitance (C) is determined from the ratio of the derivative of charge amount (Δq) to total potential range (ΔV) as shown in the following equation:

$$C = (d \times \Delta q) / (d \times \Delta V) \quad (1.8)$$

In pseudocapacitors, there are a few primary aspects such as a consistent difference of the charge with the voltage application, the lack of phase change, and the lack of diffusion restraint over a great variety of scan rates [64].

The difference between pseudocapacitor and EDLC is the reversible redox reactions formed due to the active material and electrolyte solution. A typical pseudocapacitor is schematically explained in Figure 1.11.

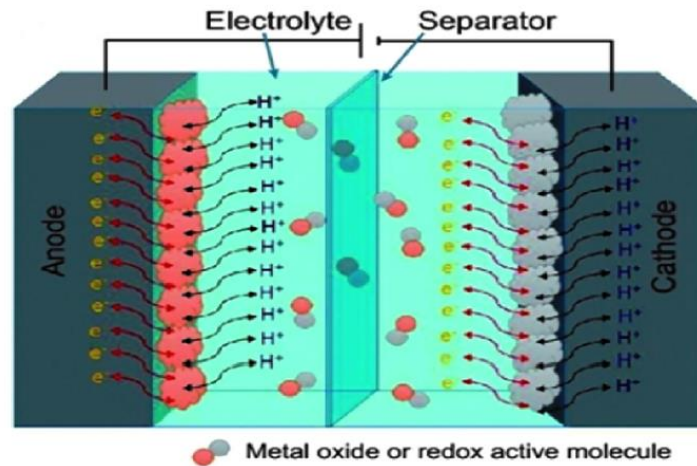


Figure 1.11. Schematic presentation a typical pseudocapacitor [50].

Pseudocapacitor contains current collectors to collaborate with the electrodes, which are inserted into an appropriate electrolyte solution. The pseudoelectrode potential is proportional to the stored charge to provide a sorption in continuous logarithmic function. Therefore, the charge stored and its corresponding voltage of electrodes used in pseudocapacitor are proportional with each other. This linear relationship induces to charge storage process depending on electron transference rather than charge gathering of the ions.

The diffusion accompanied by voltage is the main point of the Faradic reactions to arise. The pseudocapacitance is achieved from the potential magnitude of the attainable area of

adsorbed ions. Besides, chemical affinity and morphology of the active material are important to enhance the pseudocapacitive performance [50].

In pseudocapacitors, most of the charge is transferred to the bulk or electrode surfaces. Thereby, interactions between the solid material and electrolyte include a Faradaic reaction, which counts on the applied voltage. Hence, pseudocapacitor working mechanism is voltage-dependent.

Pseudocapacitors have much higher specific capacitance than EDLCs because of the existence of redox reactions. On the other hand, the power performance of pseudocapacitors is relatively lower owing to the poor conductivity and slower redox reactions during charge and discharge, leading to deficiency of cycle life [65].

1.6.2.1. Pseudocapacitive electrode materials

In general, metal oxides, conductive polymers, carbonous hetero-atoms, and other transition metal oxides exhibit pseudocapacitive features [64]. Among these materials, transition metal oxides are considered the most effective option to use in for the pseudo-electrode material in consequence of their high electrochemical performance like high power density, high energy density, long lifespan and high rate capability. There are lots of transition metal oxides like RuO_2 , $\text{Ru}_{1-y}\text{Cr}_y\text{O}_2/\text{TiO}_2$, NiO , MnO_2 , MnFe_2O_4 , Fe_3O_4 , WC , V_2O_5 , $\text{VN}_{1.08}\text{O}_{0.36}\text{Cl}_{0.1}$, etc. which have been already investigated for energy storage applications studies. Furthermore, electroactive conducting polymers can be used as an alternative electrode material for pseudocapacitors due to the reversible and rapid Faradic reactions originated from the π -conjugated polymer chains [62]. Polythiophenes (PTs) and their derivatives, polypyrroles, polyaniline (PANI) are the most promising candidates, have good conductivity, and exhibit high charge mobility [66].

1.6.3. Hybrid supercapacitors

Hybrid supercapacitors or asymmetric capacitors, which are created from the combination of a carbon-based electrode (EDLCs) and a Faradic (pseudocapacitors) electrode, possess not only higher power density but also enhanced specific energy for high rate and long-life energy storage applications [26].

Supercapacitors suffer due to their relatively lower energy density which results from limited cell potential. Therefore, hybrid supercapacitors have been fabricated to increase

the operating potential by using a pseudocapacitor and an EDLC as a positive component and negative component, respectively. Correspondingly, energy density has been improved with the increment in cell potential. Furthermore, the combination profits higher capacitance that is about two or more times more than those of other types of supercapacitors [23].

The storage mechanism of hybrid supercapacitors is principally controlled by both pseudocapacitor storage mechanism and the EDLC storage mechanism. This combined system overcomes some of the limitations derived from the each of individual capacitors and enhances the electrochemical performance [50]. Two different electrochemical processes related to the redox reactions and adsorption of ions are simultaneously carried out in the same system. The pseudocapacitive electrode possesses as energy output source, but its durability and rate performance are not acceptable. The second electrode based on non-Faradaic charge transfer where stores the charge at the double layer with a rapid response to the voltage differences, is considered as power output [67]. An illustration of a hybrid supercapacitor is given in Figure 1.12.

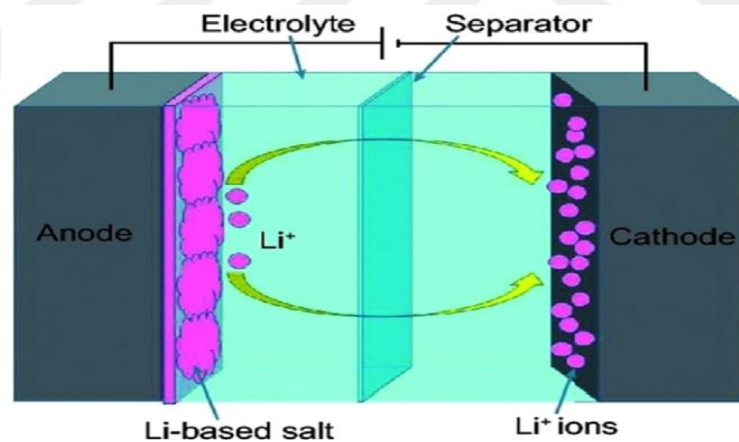


Figure 1.12. A conventional representation a hybrid supercapacitor [50].

There are two kinds of hybrid capacitors called symmetric and asymmetric based on the configuration of the assembly. Hybrid supercapacitors, when involved two diverse electrodes including different materials exhibit better electrochemical properties compared to the pseudocapacitor and EDLC, individually. Hybrid types improve the cycle life stability and range of affordability which are the weakness of pseudocapacitors. Contrary to the symmetrical EDLC, hybrid systems lead to the electrochemical performance by attaining relatively higher cell potential. The supercapacitor composed

of the combination of two similar EDLC electrodes and pseudocapacitive electrodes is named as the symmetric hybrid supercapacitor. The commercial symmetric hybrid supercapacitor consist of two electrodes of activated carbon immersed into organic electrolyte with a working voltage up to 2.7 V. On the other hand, asymmetric hybrid supercapacitor contains two dissimilar electrodes. Activated carbon/MnO₂ and activated carbon/Ni(OH)₂ are mostly used commercial asymmetric hybrid supercapacitor types [50, 68].

1.7. Electrolytes for Supercapacitors

The electrolyte is considered as some of the most critical components for supercapacitors, composed of salt and solvent. The electrolyte provides ionic conductivity which contributes to the electrochemical performance of supercapacitors.

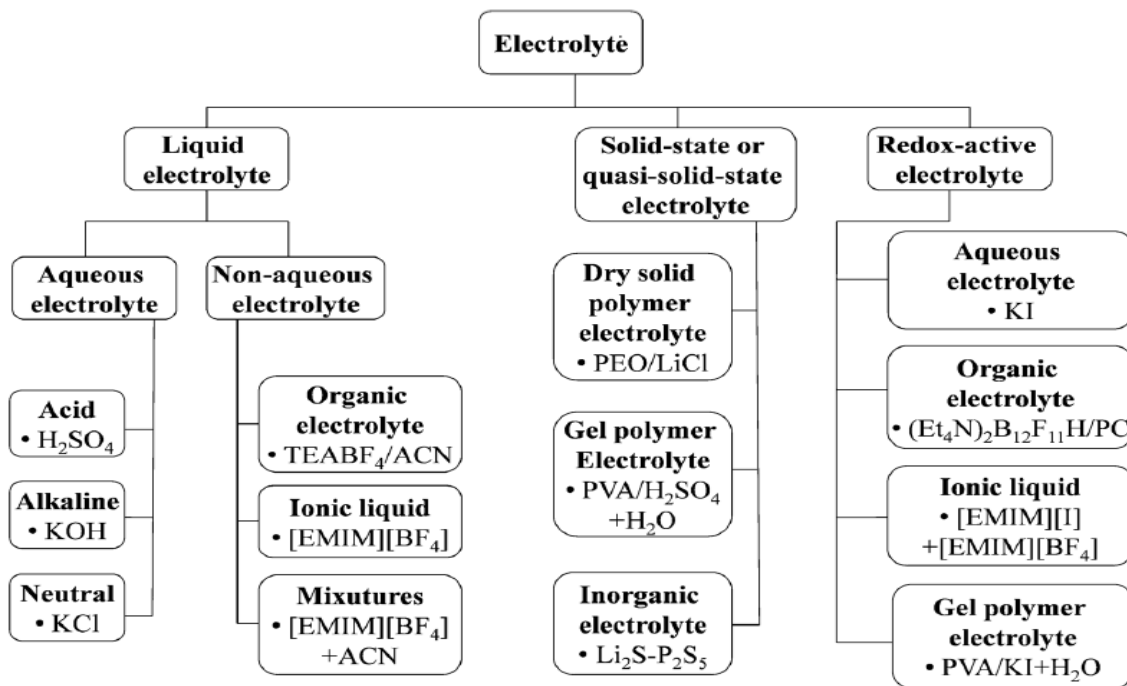


Figure 1.13. Classification of electrolytes for electrochemical supercapacitors [69].

The electrolyte type is directly related to the active material; so the choice of an appropriate electrolyte solution is very critical. The breakdown voltage of the electrolyte stands for the achievable cell voltage of a supercapacitor. To date, several kinds of electrolytes have been improved and reported in the literature given in Figure 1.13. But, two kinds of electrolytes are broadly used in supercapacitors, namely organic and aqueous

[45]. The electrolytes have both benefits and limits due to their natures. For instance, aqueous electrolytes exhibit high conductivity, resulting in high capacitance, since their working potential is restricted derived from the narrow breakdown potential of aqueous electrolytes. Otherwise, organic electrolytes can be employed at higher potentials, but their ionic conductivity is much lower than aqueous electrolytes [69].

1.7.1. Aqueous electrolytes

Among the organic and ionic liquid electrolytes, the aqueous electrolytes are superior because of lower cost, easy to operate, high ionic conductivity, and harmless to the environment. Although the aqueous electrolytes are limited owing to the working potential compared to the organic electrolytes, the ions of aqueous electrolytes are still capable of much more rapid transport rates [70].

Table 1.1 indicates the more advantageous points of aqueous electrolytes than that of organic or ionic liquid (IL) electrolytes.

Table 1.1. Electrochemical features of several electrolyte types [71].

Electrolyte	Conductivity (mS/cm)	Potential window (V)
Aqueous KOH	540	0-1
Aqueous KCl	210	0-1
Aqueous H ₂ SO ₄	750	0-1
Aqueous K ₂ SO ₄	88.6	0-1
Aqueous Na ₂ SO ₄	91.1	0-1
Organic TEABF ₄ /PC	14.5	2.5-3
Organic TEABF ₄ /CAN	59.9	2.5-3
IL, [Et ₂ MEIM] ⁺ [BF ₄] ⁻	8	4

The high conductivity of the aqueous electrolyte helps to reduce the equivalent series resistance, leading remarkably high power density supercapacitors. Apart from these properties, the size of the hydrated ionic sphere is a further substantial point to affect the electrochemical performance. The hydrated ions serve as the actual charge carriers, instead of the ions. The main acceptance is that the ions having smaller spheres improve the diffusion owing to their advanced kinetic characteristics. In addition, the smaller spheres have advantages to achieve deeper into the pores and more active sites in the

electrode materials compared to larger ones. For instance, the lithium salt is generally utilized in organic electrolytes due to having the smallest alkali metal ion. On the other hand, potassium and sodium salts having larger cations than lithium salt are mostly used in aqueous electrolytes since the hydrated K^+ and Na^+ spheres are much smaller as compared to the hydrated Li^+ sphere.

In the related applications, KOH (alkaline), H_2SO_4 (acid), and Na_2SO_4 (neutral) as aqueous electrolytes are principally preferred [71].

1.7.2. Organic electrolytes

Supercapacitor with organic electrolyte can usually possess higher energy density compared to that of with an aqueous electrolyte, because of an increased working potential range of a non-aqueous electrolytes [72]. The organic electrolyte based supercapacitors are commonly utilized in the commercial area because of their high working potential range of 2.5 to 2.8 V. With the larger working potential, the achieved energy density is significantly developed. In the literature, most studies based on organic electrolytes have been targeted on EDLCs. However, some points need to be considered in the event of preferring the organic electrolytes. Apart from the aqueous electrolytes, the organic electrolytes are expensive, lower conductive and exhibit lower specific capacitance. Additionally, they require to purify process and have safety limits such as flammability, volatility, and toxicity [69, 73].

1.8. Electrode Material Preparation Techniques

One of the most critical step is the determination of the preparation method of an electrode for the supercapacitor application, after the selection of electrode material. There are several important methods to synthesize the electrode material including sol-gel method, hydrothermal/solvothermal, chemical vapor deposition, co-precipitation, vacuum filtration, and electrodeposition.

1.8.1. Sol-gel method

Sol-gel method is so named due to the existence of micro-particles in the solution (sol) and agglomerate and collect to generate an integrated network (gel). Such an approach, polymer based substances or particularly inorganic substances are concentrated on a surface by various techniques such as solvent evaporation and continuous condensation

processes, leading to the generation of a film. Furthermore, the precursor is mixed with a liquid (water or alcohol) and the obtained solution is activated by using an acid or a base in order to react forming a network. Such a process provides the benefits of preparing materials with different composition, texture, and structures properties through the control of some parameters such as temperature, solvents surfactants types, and reaction time [74].

1.8.2. Hydrothermal/Solvothermal method

The hydrothermal method is a kind of eco-friendly superheated aqueous solution with controlled diffusion in a closed system such as Teflon-lined autoclave [75] (Figure 1.14). This method provides the active material with high purity and crystallinity. In the hydrothermal method, the solvent properties change in the case of the supercritical phase which helps to generate the particles derived from the increased reaction rate and supersaturation. However, the control capability of this method on nanoparticle aggregation is relatively lower among the other synthesis methods. When some other solvent is utilized rather than water, the technique is designated as solvothermal [33].

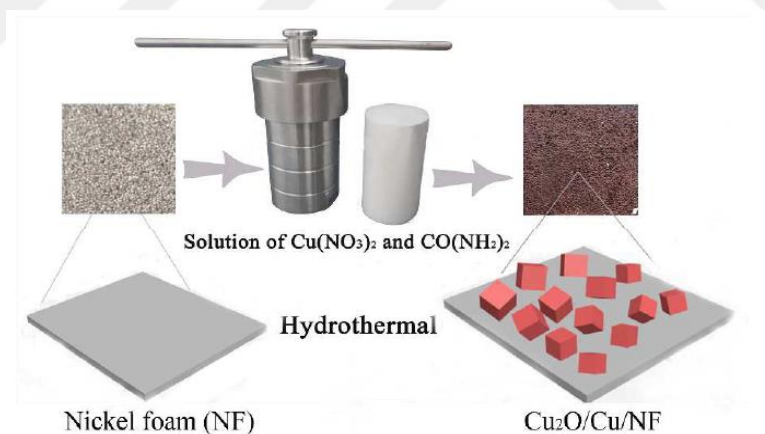


Figure 1.14. An illustration of the hydrothermal processes.

1.8.3. Chemical precipitation method

The principal point of the chemical precipitation approach is the generation of a solid powder from a solution as a result of a reaction. The solid powder can be generated from a suitable solution by two different techniques. The first one is the conversion of materials into an insoluble form and the second one is arranging the solvent composition to decrease the solubility of the material in it.

1.8.4. Chemical vapor deposition

Such approach is conducted under the vapor phase in a reactor chamber as shown in Figure 1.15. Therefore, the solution including active material is first undergone to very high-temperature treatment to be vaporized. The vaporized solution accumulates on the surface of the substrate at room condition by the condensation process, resulting in the desired solid film or powder due to the reaction or decomposition on the substrate surface. The volatile by-products occurred at the result of the process are discarded with the help of flowing gas via the reactor chamber.

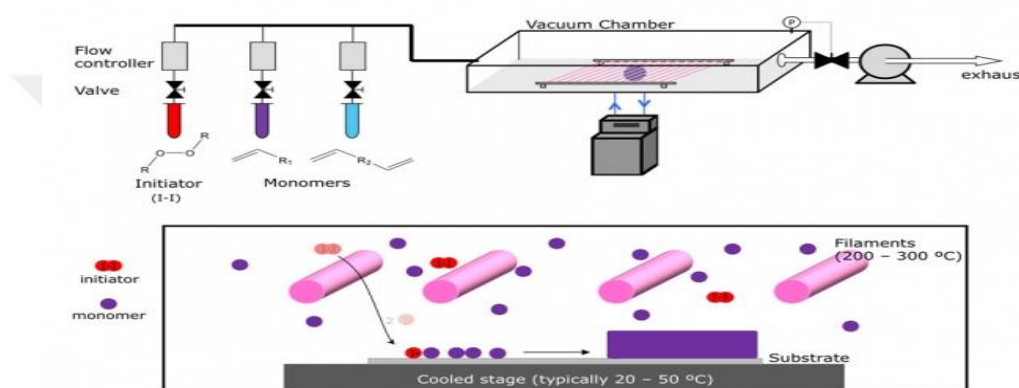


Figure 1.15. The scheme for chemical vapor deposition for electrode fabrication.

1.8.5. Vacuum filtration method

In the vacuum filtration method, nanocomposite particles are produced from the mixture of different materials by the vacuum filtration followed by a drying stage of the filtrate. With this method, the composition of the targeted product can be arranged by changing the concentration or the weight ratio of each component in the mixture.

1.8.6. Electrodeposition method

With the electrodeposition method, a film is generated on a substrate material surface by a potential application. As the well-defined potential range is applied to the electrolyte solution involving the salt of the substance to be loaded, the oxidation and reduction reactions occur which leads to film production. In such a method, the ions due to the salt which is positively charged appeals to the cathode. After arriving the substrate surface, the ions acquire the electrons from the substrate, resulting in the reduction reaction to produce the targeted material. A basic electrochemical cell which can be in two-electrode

or three-electrode configuration is used to carry out the electrodeposition technique [1]. An illustrative of a three-electrode system is represented in Figure 1.16.

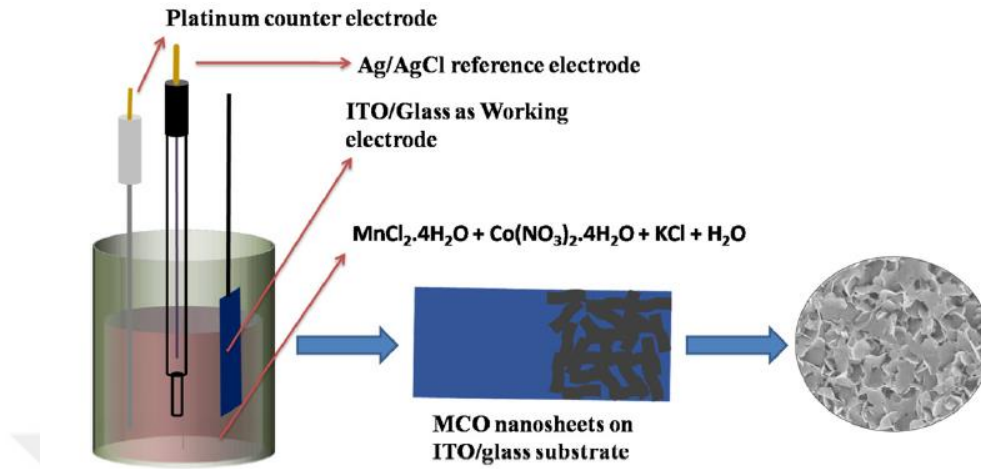


Figure 1.16. The representation of a traditional three-electrode system [1].

The advantages of the electrodeposition technique are listed [51]:

- low investment costs
- mass production in the form of effective thin films
- precise control on the structure of the active material by adjusting the parameters such as thickness, uniformity, and deposition rate.

1.9. Characterization Techniques

1.9.1. X-ray diffraction (XRD)

One of the basic approaches for the identification substance structure is X-ray diffraction (XRD). XRD technique helps to recognize the various features of the material such as phases, crystallite size, lattice strain, crystallographic texture, and defects. In the mechanism of XRD measurement, firstly electrons are produced by heating the filament in cathode ray tube with the help of potential applications. Thus, the electrons move toward the targeted substance and the substance is exposed to an attack. The X-ray spectra is generated when the incident beam provides the adequate energy to remove the electrons of the inner layer of the targeted substance. After having diffracted from the material, the X-ray pattern detected and estimated by the detector. For instance, in traditional XRD measurement of a thin film, X-rays intrude on the film surface and are diffracted into a

range of angles. These diffracted X-rays creating Bragg peaks are then collected (Figure 1.17a). This process has typically been performed in series; however, it is conducted in parallel by using an area detector, nowadays [76]. The typical XRD pattern of the film is employed by drawing a graph, intensity versus angle (Figure 1.17b).

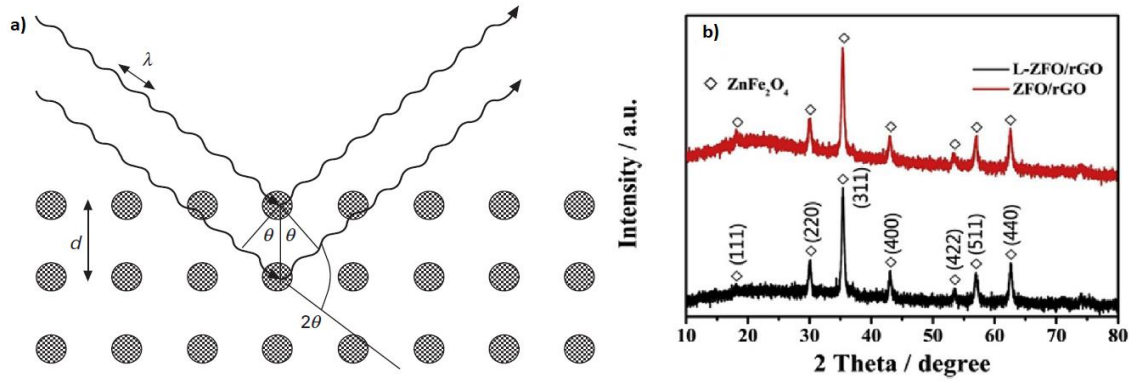


Figure 1.17. a) Schematic representation of Bragg diffraction; b) The typical XRD pattern of a film.

Diffraction arises from periodic structures that are brightened with the light of a wavelength proportional to the scale of the materials, observing for visible light by a diffraction grating. Because of the X-rays with wavelengths of $\sim 1 \text{ \AA}$, they can diffract the substances having periodic spacing related to Angstroms. The diffraction takes place through constructive interference in case the distance that exists between two rays of light (reflected from the surface of the material and the interlayers of it) becomes equal to an integer multiple of the wavelength. This approach declares with the Bragg's Equation:

$$2d \times (\sin\theta) = n\lambda \quad (1.9)$$

where θ is half of the scattering angle, λ states the wavelength of the X-ray light, n is the positive integer, and d denotes the d-spacing between the diffracting planes.

1.9.2. Raman spectroscopy

Raman spectroscopy is a quite vital and useful approach that can quickly identify samples without any destruction on their structure. Raman spectroscopy is fundamentally similar to infrared (IR) absorption spectroscopy due to their mechanism based on molecular vibrations. Consequently, both techniques provide similar information, helping to determine the structure of the material. In contrast to IR spectroscopy, in order to for a

molecule to have a Raman effect, the vibrations should lead to an alteration of polarization potential, that is, distortion of the electronic cloud. Additionally, with the Raman spectroscopy, some of the information on the material can be provided such as crystal structure, polymorph forms, phase transitions, etc. This technique is sensitive on a wide range of order scales; thus it is quite favorable for materials in all forms, excluding metals.

The Raman effect appears in case a photon is incident on a molecule and interacts with the dipole of it. The scattering related to quantum mechanics is explained as an excitation to a virtual state with lower energy compared to the energy difference of two vibrational states. During the scattering process, the molecule of the sample is excited to a virtual state, but gets promptly back to the ground state, following the re-emitted of the light. In the case of the scattered light, most of the photons diffuse without any alteration in energy, so this situation is called Rayleigh scattering, represented in Figure 1.18. However, a small number of photons, scattering non-elastically has a change in energy generated from the energy of characteristic vibrations, properties of the molecule. Thus, if the energy of the scattered light is lower compared to the incident light, this is named as Raman–Stokes scattering and on the contrary, it is denoted as the Raman–anti-Stokes scattering [77].

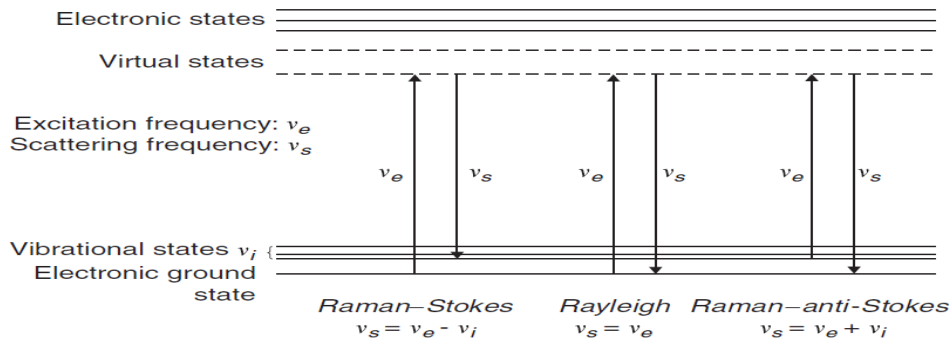


Figure 1.18. The stages of the scattering process [77].

1.9.3. X-ray photoelectron spectroscopy (XPS)

The photoelectron energy is associated with the electronic structure of the atoms.; therefore, the physical features of the material can be studied by using X-ray photoelectron spectroscopy (XPS) which is a successful method. In the case of depleting the photonics, the emissions properties change according to several factors such as the nature of the luminescent material, on its chemical state, on the host chemical composition and structure, on the presence of defects, etc. Furthermore, production technique, heat

application, and any kind of processing affecting the dopant and host energy levels broadly affect the material photoluminescence. In this technique, a material is irradiated with monochromatic x-rays which leads to the emission of photoelectrons. Such photoelectrons have characteristic energy for each element, helping to investigate the material structure. Thus, XPS is widely performed to detect the electronic structure of the elements and their oxidation state. It is further beneficial to determine the composition of a substance corresponding to the specified entire elements in the related material together with their atomic concentrations [78].

1.9.4. Scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) is a substantial approach that is broadly employed to evaluate the morphology and composition of a substance. The practical method of SEM enables the detailed three-dimensional topographical image of a material. The schematic representation of SEM involving several apparatus is given in Figure 1.19.

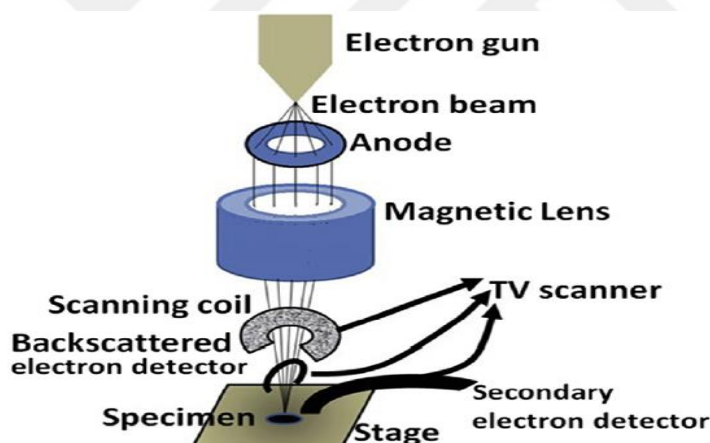


Figure 1.19. Schematic representation of scanning electron microscopy components [79].

The electrons are created at the top of the column and move downwards in which they achieve to lenses (one or two in series) in order to generate a fine beam of electrons. The incident beam of electrons strikes the sample surface received to a portable stage under vacuum condition. With the help of an electron beam, the surface of the material is scanned successfully. Considering to the interaction between the electron beam and the material, various signals are produced. These signals are detected by highly special detectors, resulting to generate images of the material [79].

1.9.5. Energy dispersive spectroscopy (EDS)

This technique facilitates a quantitative analysis by the detection of X-rays emitted from the material being tested due to the electron bombardment. Thus, this method is to help to describe the chemical composition of different elements in a specific substance according to the intensities of observed peaks. Because, in an EDS spectrum, unique peaks are detected corresponding to each element having a unique atomic structure.

1.10. Electrochemical Measurements Analyses

1.10.1. Cyclic voltammetry (CV)

This technique is an analytical tool involving the electron transfer process. It is readily employed on estimating the electrochemical behavior of a great variety of materials, especially reduction potential in a suitable solution. The cyclic voltammetry method helps to identify the relationship between the structure, potential, and electrochemical properties of the substance. Furthermore, this method is easy to perform, fast, very sensitive, and low-cost compared to other methods; therefore, it is widely used in versatile applications such as investigation of redox couples in a chemical reaction and preparation of surface coatings [80, 81].

In the cyclic voltammetry technique, the applied potential is changed over time and the corresponding current through a circuit is monitored. After oxidation/reduction occurs at the characteristic potential derived from the material nature, the current starts to flow. A typical cyclic voltammetry diagram of redox-active material is plotted to current versus applied potential at various scan rates, shown in Figure 1.20.

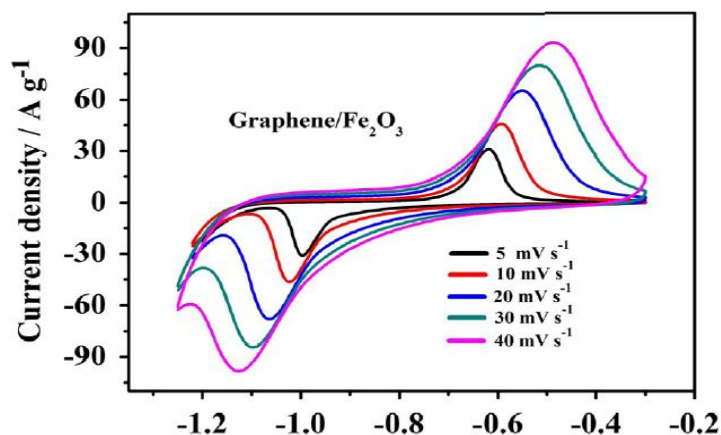


Figure 1.20. A typical cyclic voltammetry plot [82].

1.10.2. Galvanostatic charge/discharge (GCD)

The galvanostatic charge/discharge method is generally utilized to estimate the specific capacitance of an electrode material or device such as battery and supercapacitor [83]. Additionally, the cycling stability of the mentioned above devices can be investigated by this technique after thousands of charge/discharge cycles [84]. The working mechanism of this technique is quite simple that depends on applying a fixed charging current until the maximum potential is achieved. Then the subsequent stage is that a discharge current being equal with charging current is employed to a minimum potential. In this technique, the changes in voltage is monitored depending on time due to the operation of a constant current instead of a constant potential scan rate as in cyclic voltammetry. Figure 1.21 indicates the typical charge/discharge plot according to changing in current density.

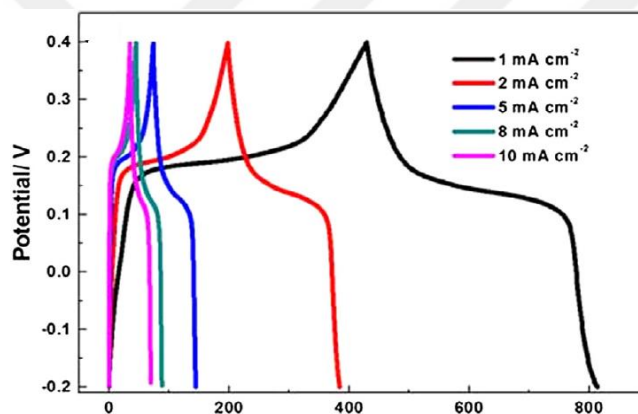


Figure 1.21. A typical GCD plot at diverse current densities [84].

1.10.3. Electrochemical impedance spectroscopy (EIS)

Such method is preferred in many areas for versatile purposes such as corrosion analysis, adsorption capability of molecules. It can further provide significant information about the physical and electrochemical features of materials such as diffusion coefficients, electron transfer rate constants, charge transfer resistance, and porosity, affecting the performance. In addition, this method is successful to recognize the changes in the conductivity of a system [85].

1.11. Literature Review

Supercapacitor is divided into two groups based on the charge storage mechanism, namely pseudocapacitors and electrochemical double-layer capacitors. The charge

storage in EDLCs is carried out through the ions adsorption/desorption at the interface of electrode and electrolyte. However, the charge storage in pseudocapacitors is conducted by reversible faradic reactions on the electrode surface. Therefore, the electrochemical performance of pseudocapacitors is more attractive as compared to EDLCs. The supercapacitor performance can be tuned with the electrode material and its composition. Carbonous materials are applied for the preparation of EDLCs, while transition metal oxides and/or conducting polymers are generally employed as electrode materials for pseudocapacitors [86-88].

Compared to all transition metal oxides, RuO_2 is the most prominent electrode material for supercapacitors, but expensive price, and high toxicity of this material hindered its application supercapacitors. NiO as a p-type semiconductor is one of the most attractive material in several areas especially supercapacitors because of its easy availability, high theoretical specific capacity, low harmful effect on environment, and strong stability [53]. Apart from these advantages, NiO has some limits due to its poor electrical conductivity. Therefore, recent studies have been aimed to enhance its pseudocapacitive performance like forming composites as binary metal oxides, contributing to increase the conductivity [89]. On the other hand, cobalt is regarded as the best option for the synthesis of binary metal oxides with nickel because of its higher conductive ability [90]. The cobalt intent can effectively reduce the resistance of the electrode with participating in the electrochemical redox reaction, resulting from improvement in electrochemical performance [91]. With the binary system synergetic effect, not only the electrical conductivity increase but also the active site density effectively enhances [92].

To date, several techniques have been developed to synthesize the electrode material for supercapacitor applications such as solvothermal/hydrothermal, sol-gel, chemical precipitation, and electrodeposition, etc. Jiang et al. fabricated Ni_2CoO_4 as an electrode material by solvothermal method following an annealing stage at 300°C for 2 h. In this study, the working electrode was comprised of the combination of the active material, conductive agent and binder. The as-prepared electrode displayed a specific capacity of 122.5 C/g and 82.5 C/g at 1 A/g and 10 A/g, respectively and the long-term durability was determined as 78.3% after 6000 cycles at 2 A/g [93]. Zhu et al. produced NiCo_2O_4 electrode material by using the sol-gel method. The as-prepared electrode had a specific capacitance of 1254 F/g at 2 A/g [94]. Among the other methods, the electrodeposition

provides a subsequent growth of admirable substance on a suitable electrode surface with higher electrochemical performance. Furthermore, this method is remarkably more facile to be employed and a high purity of deposits can be achieved without using any binders [95]. Yang et al. improved Ni-Co hydroxide nanostructures involving different compositions were fabricated by electrodeposition technique and had a high specific capacitance of 1587.5 F/g at 0.5 A/g with a rate capability of 72.7% calculated according to 10 A/g [17].

The fabrication of metal oxides with remarkably high conductive carbonous substances like carbon black, graphite, carbon nanotube, graphene, etc. is an efficient strategy to enhance the conductivity of these metal oxides. The graphene is a much more impressive alternative for the utilization in supercapacitors, as compared to the others by reason of its high conductivity, electrochemical stability, high surface area, extraordinary mechanical features; therefore, the graphene has been a point of interest for many studies [10]. Bai et al. improved an electrode by the growth of nickel and cobalt binary metal oxides on a substrate modified with graphene. The obtained specific capacitance was determined as 1410 F/g at 2 A/g with an excellent capacity preservation of 92.1% at the end of 2500 charge/discharge period. It was reported that the graphene was contributed to enhance the cycling life stability [92]. Wang et al. further provided to synthesis of graphene oxide structure on a nickel foam, followed by a thermal reduction process which converts the graphene oxide into reduced graphene oxide. After, Ni-Co-S nanosheet arrays were fabricated by the electrodeposition technique on this modified substrate. The achieved specific capacitance was calculated as 2643 F/g at 10 A/g, indicating an enhancement compared to the pure electrode without reduced graphene oxide content [3].

2. EXPERIMENTAL METHOD

2.1. Materials

All experimental studies were carried out with highly pure chemicals without any further purification. Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Merck), Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Merck), Graphite powder (Aldrich) and Potassium permanganate (KMnO_4 , Sigma-Aldrich) were used for the material synthesis. Potassium hydroxide (KOH , Merck) was used for the electrochemical measurements. HCl and H_3PO_4 , H_2SO_4 and H_2O_2 were purchased Sigma-Aldrich, Merck, and BDH Prolabo, respectively.

Ni foam as a cathode substrate (1.6 mm in thickness) was purchased from MTI KJ Group.

2.2. Equipment for preparation of electrodes

The fabrication of electrodes was conducted in a three-electrode system by using Gamry Instruments Reference 600 Potentiostat/Galvanostat/ZRA. Ni foam as the substrate, Pt wire, and Saturated calomel electrode (SCE) acted as the working, counter, and reference electrode, respectively.

2.3. Preparation of improved graphene oxide (GO)

Improved Hummer's method has been performed for the synthesis of GO and this approach is concisely depicted below:

Firstly, 9:1 mixture comprised of concentrated 120 mL of H_2SO_4 and concentrated 13 mL of H_3PO_4 was prepared. Then, this mixture was added to a mixture of 1 g of graphite powder and 6 g KMnO_4 , resulting in a slight exothermic reaction to approximately 40°C . After that, the temperature of mixture was kept constant at 50°C under stirring for 12 hours and the temperature was kept to 50°C during the stirring process. The mixture was cooled to ambient condition and poured onto 133 mL of ice with 1 mL of 30% H_2O_2 . Then, the supernatant was removed, and the remaining solid was rinsed with deionized water (DI), acetone, and ethanol for several times by a using centrifuge. At each wash, the centrifuge was carried out at 4000 rpm for 10 minutes. Finally, the gained solid was left for vacuum drying at 40°C for 2 days, and as an end product, brown colored powder of graphene oxide was achieved.

2.4. Preparation of NCO electrodes with electrodeposition method

The electrodeposition method was practiced to prepare all the electrodes and nickel foam was served as a substrate for this process. Before the electrodeposition, nickel foams with size $1 \times 1 \text{ cm}^2$ were firstly cleaned by sonication in acetone, DI and ethanol for 5 minutes for each to eliminate the surface impurities and dried at ambient conditions. An aqueous electrolyte solution including 0.01 M Ni-precursor and 0.01M Co-precursor was prepared through stirring for 30 minutes at room temperature for performing electrodeposition. Then, the obtained transparent pink solution was transferred to three-electrode system. For the growing of Ni-Co structures on the nickel foam, cyclic voltammetry one of the electrodeposition techniques was performed at a scan rate of 50 mV/s for the various CV cycles within a voltage range of -1.5 V to 0.5 V. The achieved structures after 5, 10 and 15 scans were named as NCO-5, NCO-10 and NCO-15, respectively. The electrodeposited nickel foams were rinsed with DI and dried at 60°C for overnight, followed by annealing at 300°C for 2 h in a muffle furnace. After the annealing process, the green-colored thin film on nickel foam was converted to black colored film, given in Figure 2.1. The mass of deposited active material was found by calculating the mass difference of nickel foam after and before the electrodeposition.



Figure 2.1. The representation of color difference of as-prepared electrodes.

2.5. Preparation of NCO-RGO electrodes with electrodeposition method

Preparation of NCO-RGO electrodes occurred from two parts; optimization of graphene oxide amount and optimization of Ni-Co ratio in the electrolyte solution.

2.5.1. Optimization of graphene oxide

Preparation of the electrodes including reduced graphene oxide was done with the one-step electrodeposition method. An aqueous electrolyte solution including 0.01 M Ni-

precursor and 0.01M Co-precursor was prepared and stirred for 30 minutes. After that, various amounts of graphene oxide were added to the solution and had a sonication process for 60 minutes at room temperature. The acquired solutions containing 0.10 mg/mL, 0.25 mg/mL and 0.50 mg/mL GO were denominated as NCO(1:1)-10-rGO-0.10, NCO(1:1)-10-rGO-0.25, and NCO(1:1)-rGO-0.50, respectively. Then, the cyclic voltammetry technique was employed at 50 mV/s scan rate for 10 CV cycles (optimum value) between the voltage range of -1.5 V and 0.5 V. After drying under mentioned conditions in previous section, the samples were annealed at 300 °C for 2 hours in a tube furnace under Argon atmosphere. The fabricated electrodes were also named as NCO(1:1)-10-rGO-0.10, NCO(1:1)-10-rGO-0.25, and NCO(1:1)-rGO-0.50. The mass of active material grown on the substrate was equal to the mass difference of substrate after and before the electrodeposition process.

2.5.2. Optimization of Ni-Co ratio in electrolyte

The one-step electrodeposition method was also applied to attain six different compositions of Ni-Co coatings as NCO-RGO electrodes. Ni and Co containing precursors were mixed in different molar ratios in the presence of DI and stirred for 30 minutes to prepare the electrolyte solution. After that, graphene oxide was put in to the solution and exposed a sonication for 60 min. Graphene oxide concentration in all prepared solutions was 0.25 mg/mL (the optimum result achieved from the previous section). For the electrodeposition process, the cyclic voltammetry technique was performed at the same operation conditions mentioned above. The washing and drying procedure were the same with the former two sections. After drying, annealing stage was done similar to Section 2.5.1. These molar ratios in the electrolyte (30 mL) are given in the following Table 2.1.

Table 2.1. The mass of Ni-Co precursors and contents of GO for each corresponding electrode in the electrolyte solution.

Molar ratio for Ni/Co in electrolyte	Sample name	Ni content (g)	Co content (g)	GO content (g)
1:0	NCO(1:0)-10-rGO-0.25	0.1746	-	0.0075
0:1	NCO(0:1)-10-rGO-0.25	-	0.1742	0.0075
1:1	NCO(1:1)-10-rGO-0.25	0.0875	0.0874	0.0074
1:2	NCO(1:2)-10-rGO-0.25	0.0581	0.1164	0.0077
2:1	NCO(2:1)-10-rGO-0.25	0.0583	0.1166	0.0075
4:1	NCO(4:1)-10-rGO-0.25	0.1397	0.0351	0.0076

2.6. Materials Characterization

The structure of as-obtained electrodes were explored by X-ray diffraction (XRD, Bruker D2 Phaser X-ray diffractometer under Cu K α irradiation at $10^\circ < 2\theta < 90^\circ$). The X-ray photoelectron spectroscopy (XPS) analysis was conducted by Thermo-Scientific spectrophotometer using an Al-K α (1486.7 eV) -X-ray source with the beam size of 400 nm diameter. Raman analyses for structural study were performed by using Raman spectrophotometer STEX- 100. The surface morphology and composition of the as-fabricated electrodes were inspected by scanning electron microscopy (SEM, ZEISS EVO MA10) equipped with energy dispersive X-ray spectrometer (EDS).

2.7. Electrochemical Measurements

All electrochemical studies were employed in a conventional three-electrode cell constructed of modified Ni foam as the working electrode, Pt wire as the counter electrode, and SCE (in saturated KCl solution) as the reference electrode in 2 M KOH as aqueous electrolyte at ambient conditions. Cyclic Voltammetry (CV) tests were performed in the potential range of -0.1 to 0.5 V at various scan rates varying from 5 to 50 mV/s using Gamry Instruments Reference 600 Potentiostat/Galvanostat/ZRA. Electrochemical impedance spectroscopy (EIS) measurements were also examined by Gamry Instruments Reference 600 Potentiostat/Galvanostat/ZRA in the frequency range of 100 kHz to 0.1 Hz at a constant amplitude of 10 mV. Galvanostatic charge/discharge (GCD) measurements depending on the changing current density were done by using Gamry Instruments Interface 1000B Potentiostat/Galvanostat/ZRA.

3. RESULTS AND DISCUSSION

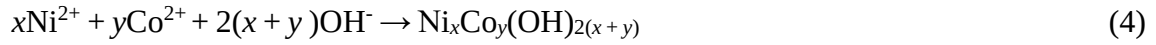
3.1. Growth of the NCO and NCO-RGO Hybrid Structures

The standard reduction potential of Nickel (-0.25 V vs. SCE) and Cobalt (-0.28 V) are very close; therefore, it is considered that both elements can be combined into the alloy in its nominal compositions. Figure 3.1 shows repetitive CV response of the electrodeposition of NCO-10, NCO(1:1)-10-rGO-0.25 and NCO(2:1)-10-rGO-0.25 in the potential range of -1.5 to 0.5 V at 50 mV/s. It is declared that cathodic current increases corresponding to the increase in the number of CV cycle, indicating the electrochemical deposition processes of nickel and cobalt components, take place particularly in the potential range of -1.0 V to -1.5 V. Except the CV curve due to the NCO-10 electrode, the CV curve of NCO(1:1)-10-rGO-0.25 and NCO(2:1)-10-rGO-0.25 electrodes include another small peak at about -0.5 V and -0.65 V, implying the reduction of graphene oxide in the electrolyte solution to reduced graphene oxide. After the electrodeposition of NCO and NCO-RGO hybrid films, the Ni foam converted into green and dark green color is visible to the naked eye, providing the electrodeposition of the related structures on the Ni foam.

The NCO nanosheets and NCO-RGO hybrids nanosheets were fabricated on a Ni foam by the electrodeposition method following an annealing process. The Ni-Co double hydroxide precursors were co-electrodeposited due to the interactions of Ni^{2+} and Co^{2+} with hydroxyl emerged from the reduction of NO_3^- . With the formation of OH^- , pH increases and the solubility of $\text{Co}(\text{OH})_2$ is highly similar to the $\text{Ni}(\text{OH})_2$ at the room temperature, introducing the homogeneous deposition of the binary Ni-Co hydroxide precursors on the substrate surface. The OH^- ions at the electrode surface are generated through the equations [18]:



Subsequently, the deposition of Ni-Co double hydroxides on a Ni foam surface is represented with the equation (4) [17, 18].



Finally, the precursors are thermally transferred into the Ni-Co binary metal oxides.

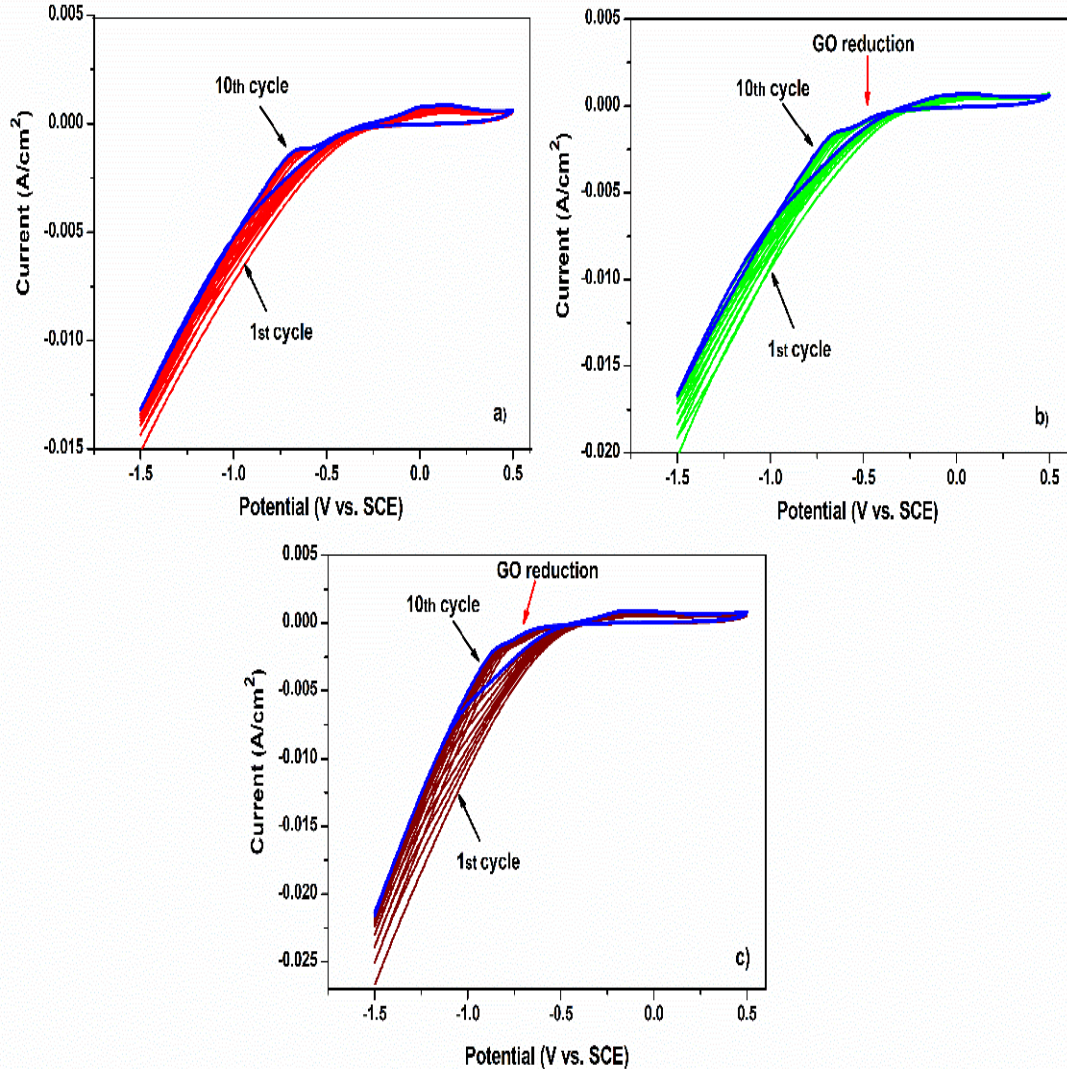


Figure 3.1. The growth of the NCO and NCO-RGO structures on the substrate by using the CV method.

After the annealing process, the mass of active material was determined from the weight difference of substrate after and before the electrodeposition. Thus, the weight of active material deposited on the substrate for all samples is given in Table 3.1.

Table 3.1. The mass of active material on the Ni foam substrate by electrodeposition method.

Sample name	Mass of active material (mg)
NCO-5	0.9
NCO-10	1.3
NCO-15	1.8
NCO(1:1)-10-rGO-0.10	0.8
NCO(1:1)-10-rGO-0.25	0.8
NCO(1:1)-10-rGO-0.50	0.9
NCO(1:0)-10-rGO-0.25	0.7
NCO(0:1)-10-rGO-0.25	0.6
NCO(1:2)-10-rGO-0.25	0.9
NCO(2:1)-10-rGO-0.25	0.9
NCO(4:1)-10-rGO-0.25	1.0

As seen from Table 3.1, the total masses of NCO-RGO hybrids on the electrode surfaces decrease as compared to the masses of NCO nanosheets at the same number of CV cycles, demonstrating the thinner coatings which helps to enhance the electrochemical performance of as-prepared electrodes for supercapacitor applications.

3.2. Characterization of NCO and NCO-RGO Hybrid Electrodes

3.2.1. Raman spectroscopy

Raman spectroscopy is a functional procedure to analyze the characterization of the lattice properties and the band structure of a material, as well as crystallinity. In this study, this method is practiced for the demonstration of the existence of as-prepared GO, NCO-10, and NCO(1:1)-10-rGO-0.25 films. In the Raman spectra, the presence of GO can be verified by two distinct peaks designated with D and G bands, respectively. As illustrated in Figure 3.2, the D band detected at 1357 cm^{-1} arises from the structural disorders of the GO-nanocomposite structure, while the G band with the position of 1600 cm^{-1} is attributed with the vibrations of sp^2 bonded carbon atoms in both rings and chains. Furthermore, the intensity ratio (I_D/I_G) is an indicator to determine the mean particle size of sp^2 carbon atoms and defects degree in carbonous materials; thus, the intensity ratio of

I_D/I_G is calculated to be 0.65 is relatively closer to reported previous works [55]. As displayed in Figure 3.2, the two peaks corresponding to the NCO are located at 506 cm^{-1} and 681 cm^{-1} which is confirmed by the related literature [92, 96]. On the other hand, for the hybrid electrode, two different peaks are also observed at 1345 cm^{-1} and 1605 cm^{-1} , which are assigned to the D band and G band originated from the RGO, respectively. Additionally, the position of peaks due to the NCO is found to be 470 cm^{-1} and 533 cm^{-1} , respectively. All Raman peaks assigned to RGO and NCO in the structure of the hybrid electrode shifted to the left compared to that of GO and NCO. Such observation can be attributed the formation of the desired composite layer on Ni foam by the chemical interaction [97]. The integrated ratio between the D and G bands is determined as 1.00 which is higher than the graphene oxide. Thus, the Raman spectrum of the as-obtained samples reveal that the average number of sp^2 hybrid carbon atoms decreases, indicating the reduction of GO to RGO, confirming reported works [10].

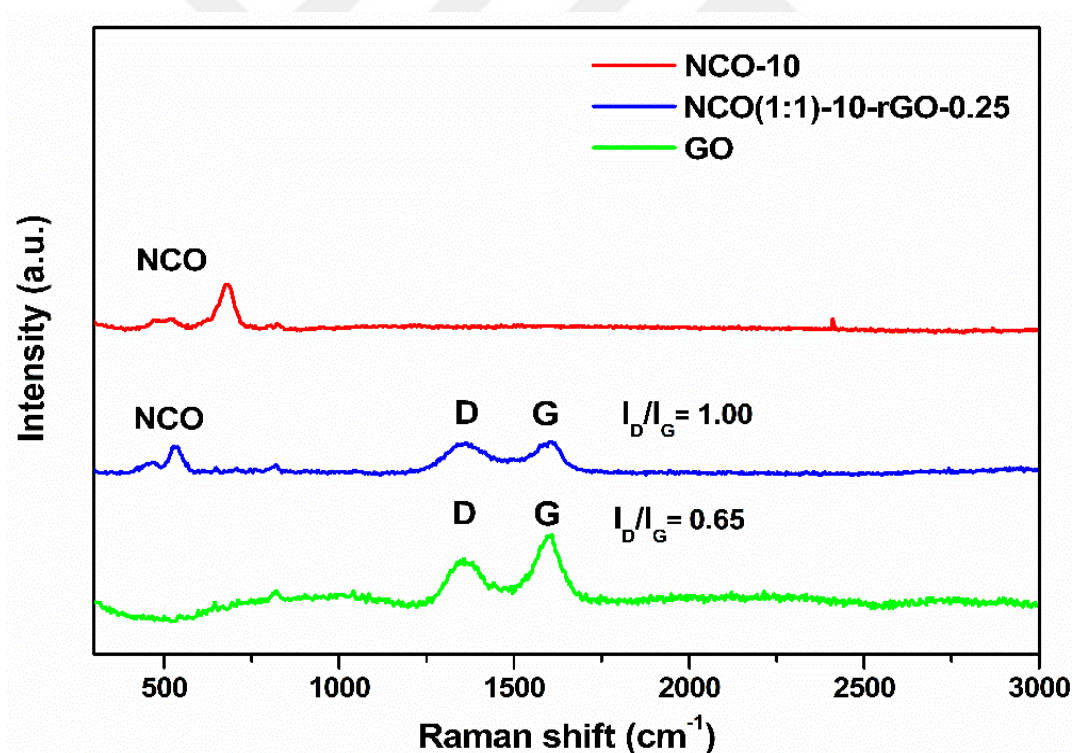


Figure 3.2. Raman spectrum of NCO and NCO-RGO nanosheets.

3.2.2. X-ray diffraction

XRD has many advantages to determine the dimension of crystal size and the chemical formula of fabricated products. To confirm the structural phase composition, the XRD patterns of as-obtained samples on Ni foam are demonstrated in Figure 3.3. The diffraction peaks at the 2θ values of 44.6° , 51.9° and 76.6° matched patterns planes of the face-centered cubic (fcc) Ni phase (Powder Diffraction File No. 040850, Joint Committee on Powder Diffraction Standards, [2004]) corresponding to (111), (200) and (220). On the other hand, NCO and NCO-RGO characteristic peaks have clearly not appeared which can be attributed to the formation of quite thin layered nanosheets and domination of high intense peaks due to the Ni foam or their amorphous phase nature. These results are in conformance with the previous works [2, 6, 98]. Besides, XRD patterns of NCO and NCO-RGO slight shift compared to Ni foam which can be an evidence to form a layer composed of Ni-Co-RGO on the surface of Ni foam.

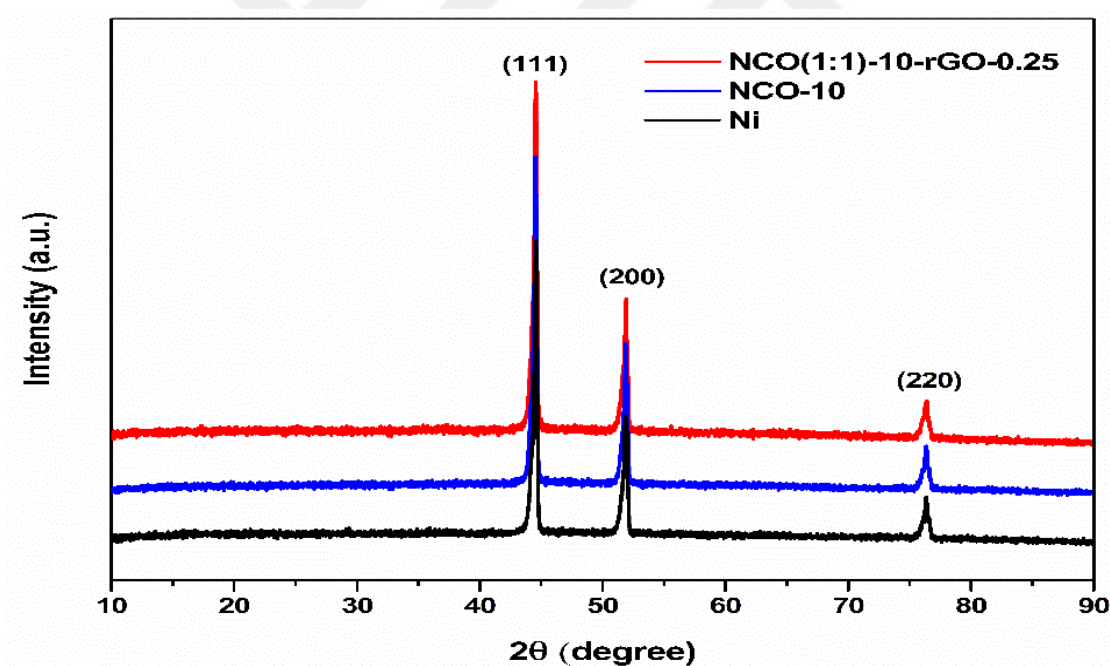


Figure 3.3. XRD pattern of as-obtained products grown on Ni foam.

3.2.3. X-ray photoelectron spectroscopy

XPS analysis was employed to figure out the composition and the oxidation states of the elements of as-obtained nanosheets. The typical survey spectra reveals that the electrode of NCO(2:1)-10-rGO-0.25 is primarily composed of Ni, Co, O, and RGO (Figure 3.4).

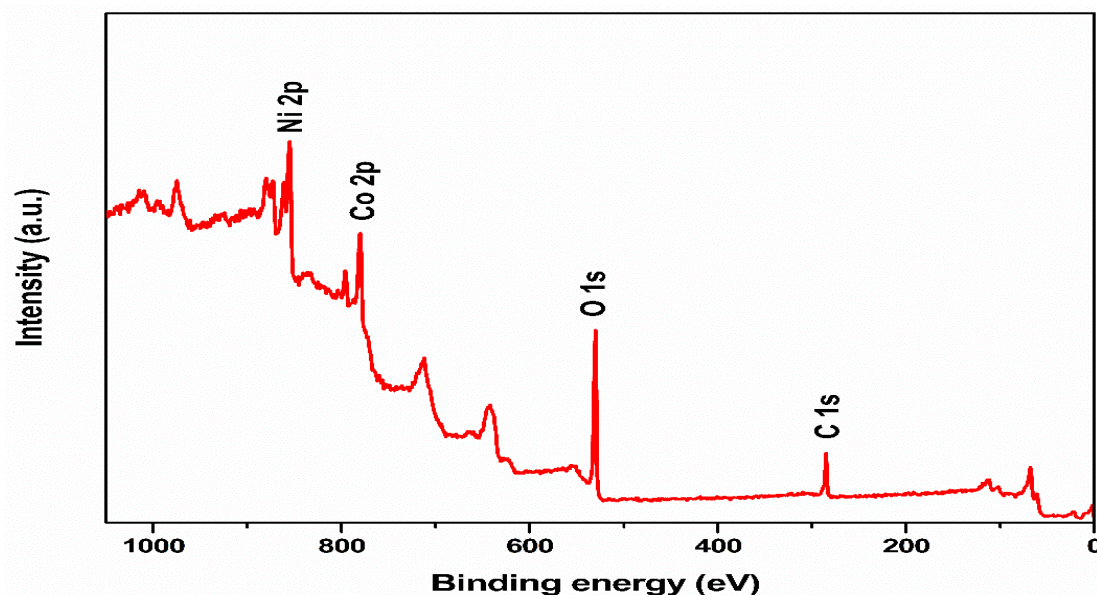


Figure 3.4. Representative XPS survey spectrum of NCO(2:1)-10-rGO-0.25.

Figure 3.5a shows the core-level of Ni 2p spectra which involves two prominent peaks with spin-orbit binding energies located at 873.1 eV and 855.2 eV correspond to Ni 2p_{1/2} and Ni 2p_{3/2}, respectively. The main peak of Ni 2p_{3/2} and its satellite peak is related to Ni²⁺ and Ni³⁺ oxidation states [99]. Furthermore, two satellite peaks (indicated as Sat.) at around 879.5 eV and 861 eV are two shakeup type peaks of nickel, at the high binding energy sides of Ni 2p_{1/2} and Ni 2p_{3/2}. Similarly, the Co 2p spectrum has also two main peaks of Co 2p_{3/2} at 780.2 eV and Co 2p_{1/2} at 795.4 eV along with two shakeup satellites at 803.8 eV and 788.9 eV. The major peak of Co 2p_{3/2} and its satellite are associated with the Co²⁺ and Co³⁺ oxidation states [99] (Figure 3.5b). In the O 1s XPS spectrum (Figure 3.5c), one peak is observable located at 530.1 eV assigned to the metal-oxygen bonds [100]. In general, the XPS spectra of GO has four peaks at 283, 285, 287, 282 eV associated with carbon atoms in form of C-C (sp² carbon), C-O (carbonyls), O-C=O (carboxyl) and C-OH (hydroxyls), demonstrating the presence of surface functional groups [101]. However, the C1s spectrum shows just two peaks at 285.0 (C-C/C=C bonds) and 288.2 eV (O=C-OH) which is an evidence for the existence of RGO derived from the depletion of most of oxygen involving groups in the electrochemical reduction of GO (Figure 3.5d). Obviously, the XPS measurements clearly demonstrate that the as-fabricated materials have a mixed composition, containing Ni, Co, O, and C which well matches the phase of NCO-RGO hybrid metal oxides.

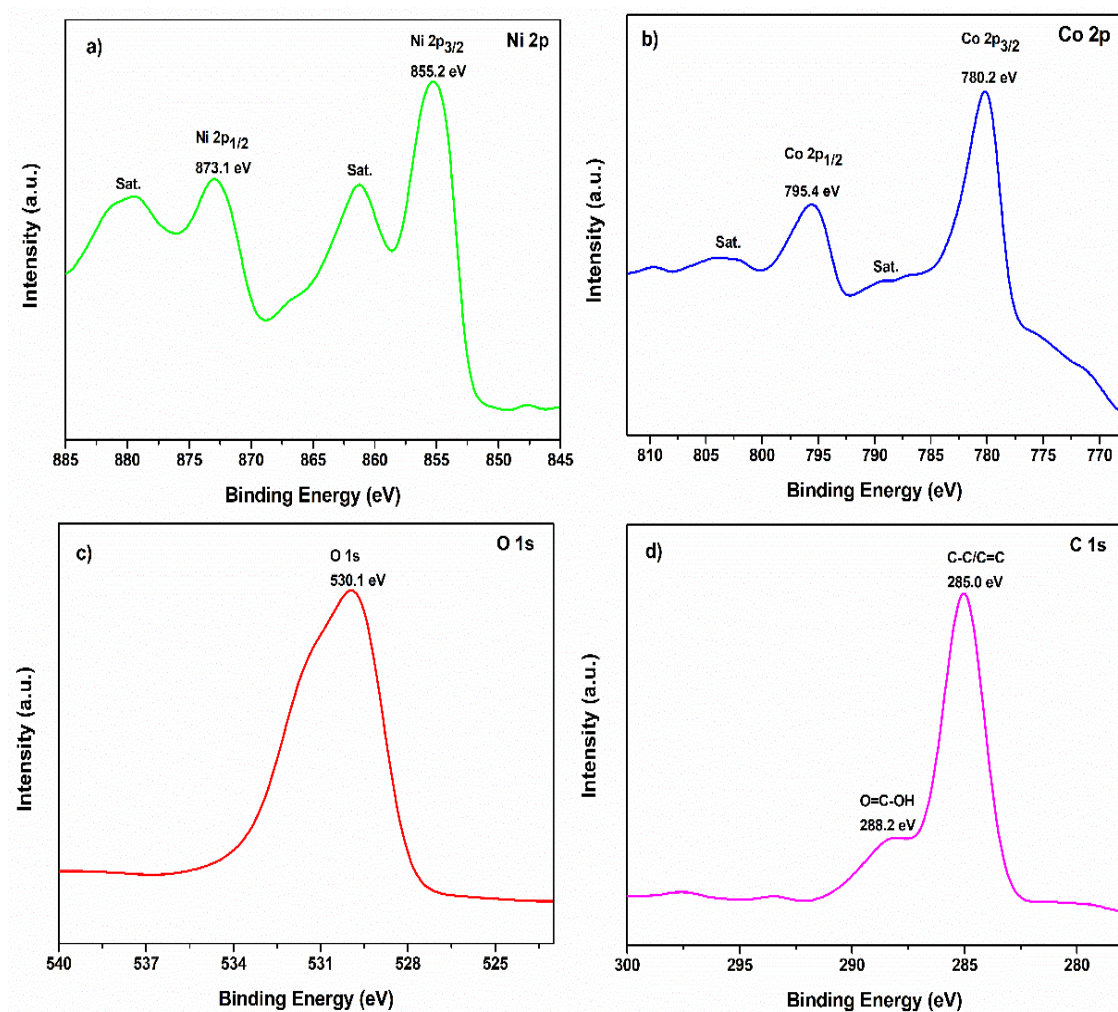


Figure 3.5. XPS spectra of NCO(2:1)-10-rGO-0.25 electrode a) Ni 2p; b) Co 2p; c) O 1s; d) C 1s.

3.2.4. Scanning electron microscopy

SEM is a versatile approach that helps to explore the morphology and structure of the as-fabricated materials. Figure 3.6 indicates the SEM images of the fabricated various nanosheets on the Ni foam as substrate. It can be clearly seen that the morphology of NCO(1:0)-10-rGO-0.25 has huge agglomeration in places (Figure 3.6a). However, in the presence of Co ions in the electrolyte solution (Figure 3.6 b-c), the agglomerated appearance has decreased and converted into a lamellar structure with folds which enables to develop the electrochemical performance of material due to the expansion of the surface area.

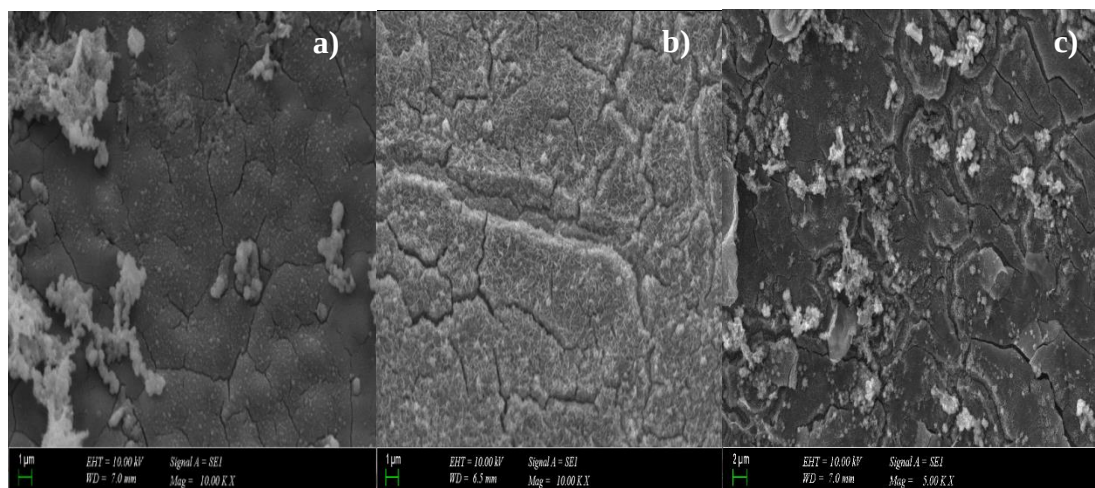


Figure 3.6. Low-magnified SEM images of a) NCO(1:0)-10-rGO-0.25; b) NCO-10; c) NCO(1:1)-10-rGO-0.25 hybrid electrodes.

The low-magnification scanning electron microscopy image indicates that the hybrid nanosheets composed of binary Ni-Co metal oxide and RGO are uniformly loaded onto Ni foam scaffold as seen in Figure 3.7a. Ultrathin reduced graphene oxide layers were coated on the surface of substrate through the reduction of GO with simultaneous electrodeposition of the related films and displayed ripple-like wrinkles, implying the close contact between reduced graphene oxide and Ni foam as seen in Figure 3.7b. In comparison the images of NCO-10 and NCO(2:1)-10-rGO-0.25, it can be observed that their morphology changes drastically by incorporation of the GO in the electrolyte during the electrodeposition. The electrode of NCO-10 has a low porous structure (Figure 3.7d). However, the synthesized electrodes with reduced graphene oxide exhibited vertically standing wrinkled nanosheets with thickness at the range of 25-60 nm interconnected with each other in order to form a porous network structure, leading to numerous large open spaces and electroactive surface sites, shown in Figure 3.7c presented with high-magnification. Such high porous network-like structure will undoubtedly provide to enhance the surface area, help to easy access for ions at the interface of active material and electrolyte and shorten the diffusion way to improve the reaction kinetics and the electrochemical performance [102]. As seen in Figure 3.7e, the thicknesses of layers on Ni foam are considerably thin changing from 910 nm to 1.66 μm which is beneficial for enhancement of the supercapacitive performance.

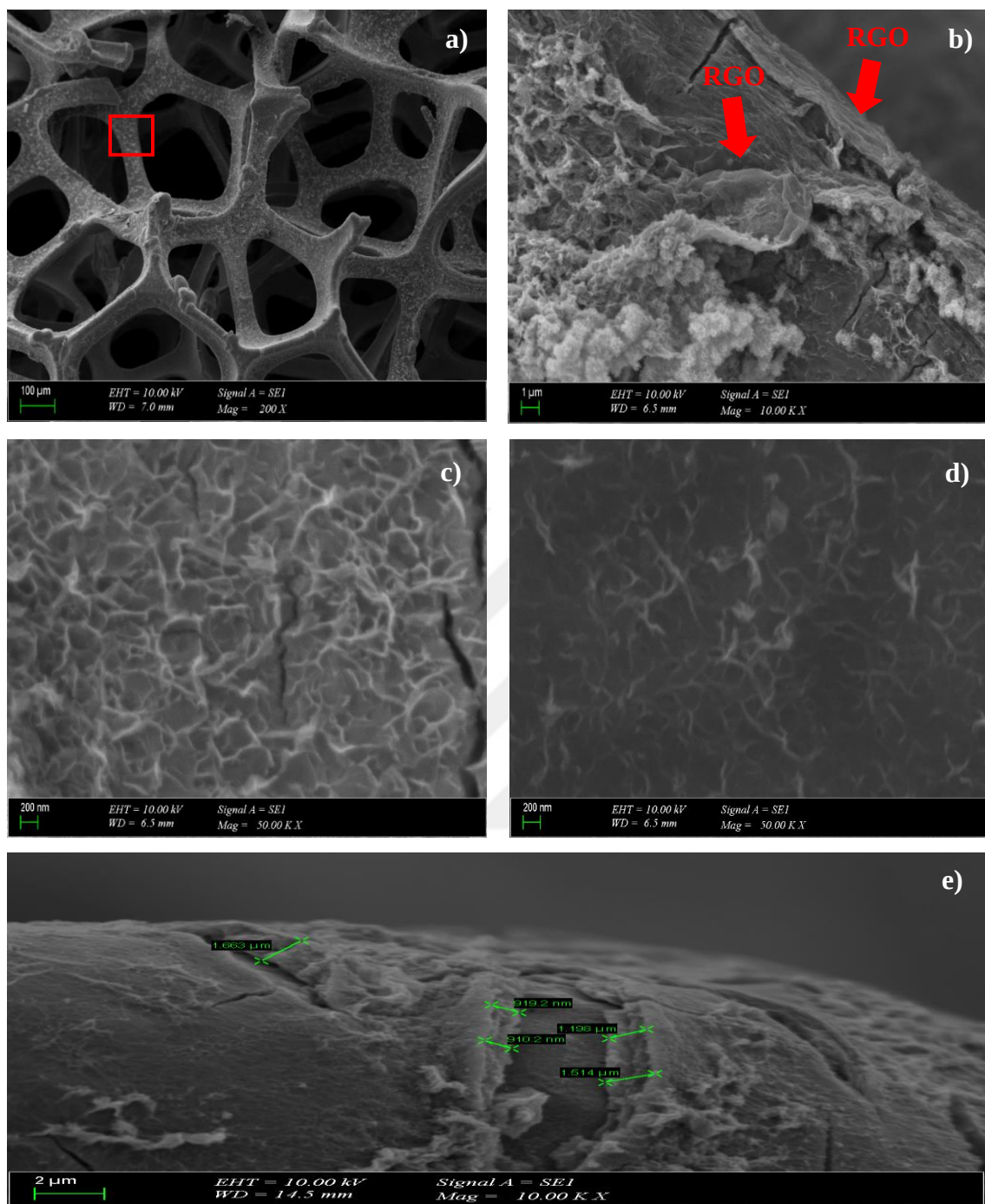


Figure 3.7. Structure and morphology of nanosheets a) low and (b,c) high-magnified SEM images of NCO(2:1)-10-rGO-0.25; d) high-magnified SEM images of NCO-10; e) thickness of NCO(2:1)-10-rGO-0.25 layer on Ni foam.

3.2.5. Energy dispersive spectroscopy

EDS analysis was performed to study the composition of the as-prepared electrode and it revealed a few peaks corresponding to nickel, cobalt, oxygen, and carbon which confirms

the successful formation of the related structure on the surface on the Ni foam (Figure 3.8). The signals of Ni, Co, and O come from the nickel-cobalt oxide and the existence of signal due to C element indicates the presence of reduced graphene oxide in the structure which are further confirmed by the XPS results. The deposited molar ratio of Ni:Co was estimated to be 1.9:1 which is close to the feeding ratio of 2:1 and can be supported with the previous studies [92]. The EDS results show that the samples are good agreement with their elemental signals and the stoichiometric ratio is calculated as expected.

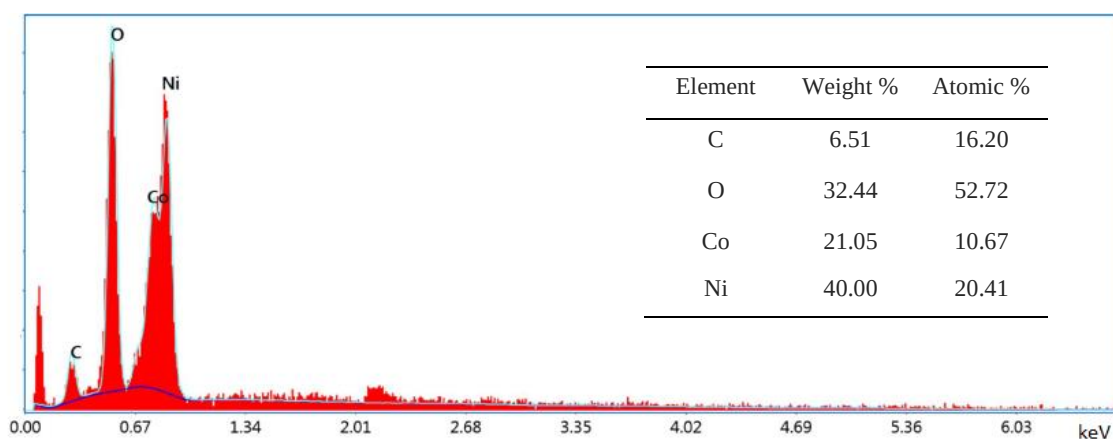


Figure 3.8. EDS spectrum of NCO(2:1)-10-rGO-0.25 with inset showing percentage of elements.

3.3. Electrochemical Behaviors of NCO Electrodes

3.3.1. Cyclic voltammetry (CV) analyses

CV measurement is an important approach to find out the redox potentials of components and the reversibility of the reaction. CV analyses were practiced to investigate the electrochemical properties of fabricated films on Ni foam in a conventional three-electrode configuration using 2 M KOH as the electrolyte solution. CV tests were done at various sweep rates changing between 5 to 50 mV/s in a voltage window of -0.1 to 0.5 V to evaluate the effect of the scan rate on the electrochemical behavior. CV measurements were examined for NCO-5, NCO-10, and NCO-15 electrodes, and the results are represented in Figure 3.9. As seen, the CV profiles of NCO sheets are approximately uniform and display a couple of redox peaks, demonstrating their strong pseudo-capacitive performance due to the Faradic reactions.

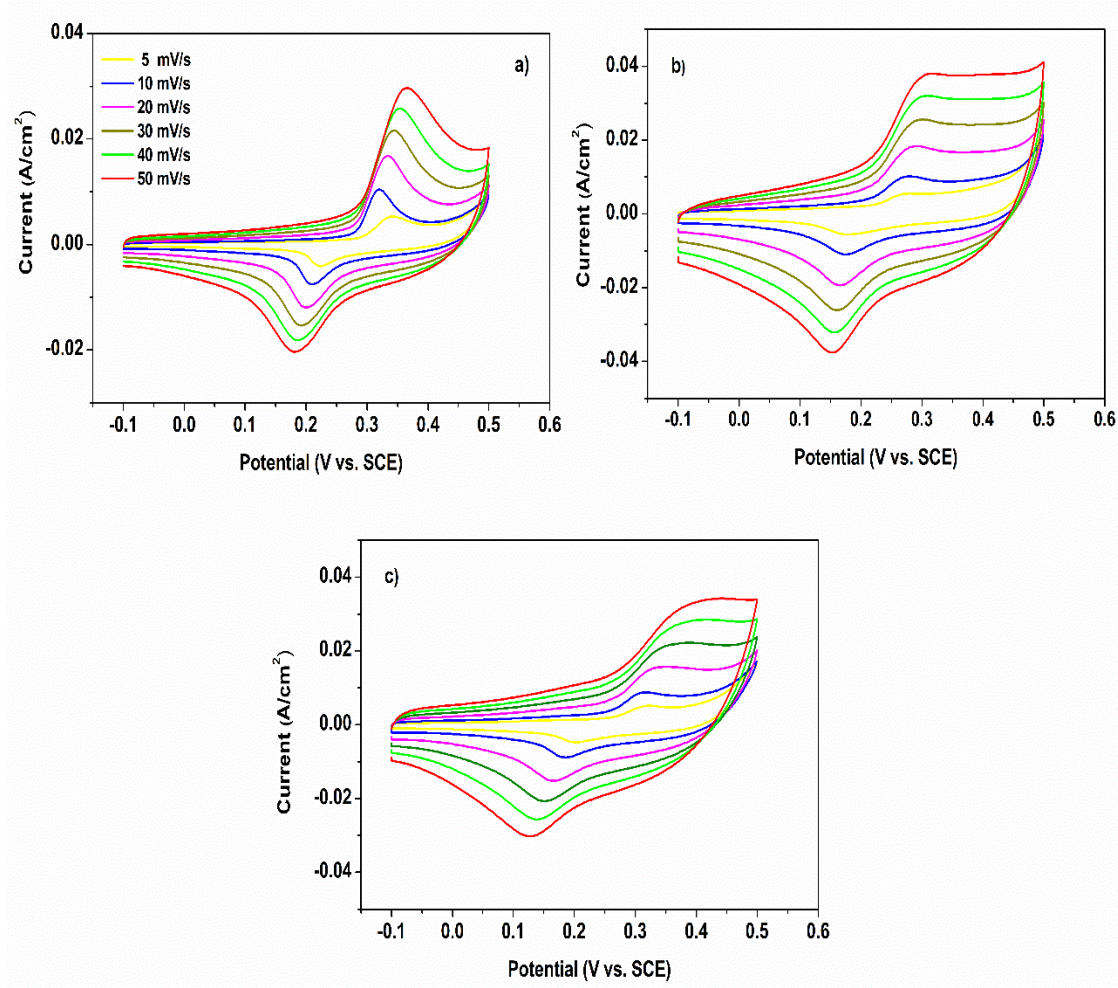


Figure 3.9. All CV profiles of as-prepared samples at various sweep rates a) NCO-5; b) NCO-10; c) NCO-15.

The anodic peak and the cathodic peak around at 0.27 V and 0.16 V state the conversion of $\text{Ni}^{+2}/\text{Ni}^{+3}$ and $\text{Co}^{+2}/\text{Co}^{+3}$, respectively. As it is seen, NCO-10 exhibits a better electrochemical reversibility as compared to the other two electrodes. Since, it is not observed a clear deviation for the reduction peak even though the peak due to the oxidation slightly shifts towards the positive potentials with the increasing scan rate derived from the redox reaction mechanism. Furthermore, it is noticeable that the peak currents corresponded to the pair of redox reactions increase directly depend upon the scan rate due to the fast charge/discharge rate by means of the ionic transportation, demonstrating their strong pseudo-capacitive performance

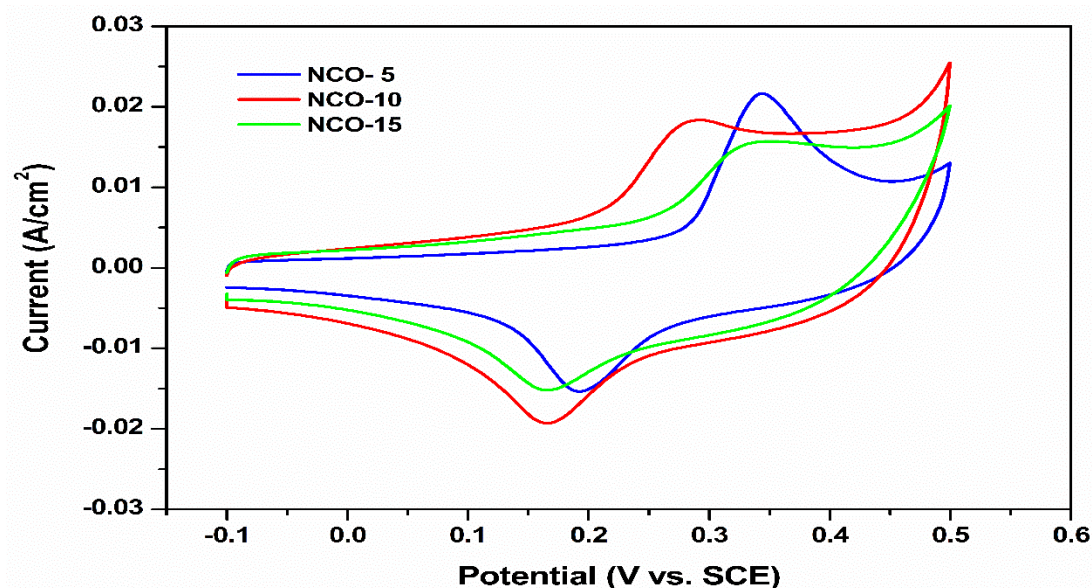


Figure 3.10. Comparison of as-fabricated electrodes at a scan rate of 20 mV/s.

In addition, it is possible to determine the specific capacitance from the area under the CV area at the sweep rate of 20 mV/s, indicating the higher specific capacitance than that of two other sheets, as seen from the Figure 3.10. However, the specific capacitance values were determined by using the charge/discharge measurements depended on the discharge current densities in detail in the following sections.

3.3.2. Galvanostatic charge/discharge (GCD) analyses

GCD measurement is a crucial approach to elaborate on the electrochemical performance of electrodes especially the determination of the specific capacitance and the lifespan. GCD analyses were performed between the potential range of 0-0.5 V vs. SCE at diverse discharge current densities varying from 10 to 30 A/g to compare the performance of the as-fabricated electrodes. Figure 3.11 shows the GCD profiles of the NCO-5, NCO-10, and NCO-15 nanosheets based on the different current densities, respectively. It is obvious that the curves are deeply symmetrical in nature suggesting the good capacitive quality. However, the capacitive performance tends to decrease with an increase in discharge current because of the slow redox reactions at high current densities originated from fast ion transportation and inadequate time for interaction between the ions and electrode surface.

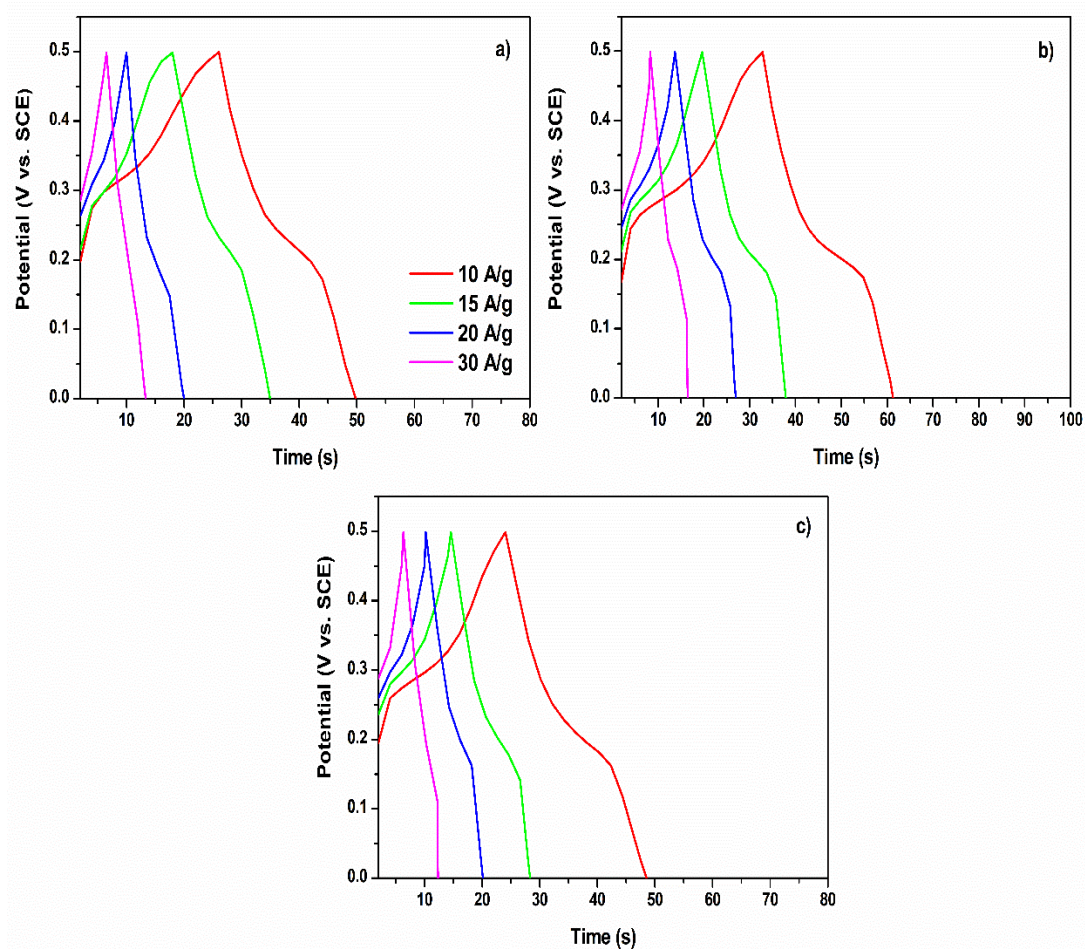


Figure 3.11. GCD curves of as-prepared electrodes based on the changing current density a) NCO-5; b) NCO-10; c) NCO-15.

The specific capacitance of the electrodes electrodeposited by cyclic voltammetry technique was estimated by using the following equation: [13]

$$C_s = (I \times \Delta t) / (m \times \Delta V) \quad (3.1)$$

in which C_s states the gravimetric specific capacity (F/g), i is the discharge current (A), Δt denotes the discharge time (s) and m is the mass of the deposited active materials on the substrate (g). The determined specific capacitances of all prepared electrodes at various current densities are given in Table 3.2.

Table 3.2. The specific capacitances of as-fabricated electrodes at diverse current densities.

Discharge Current Density A/g	NCO-5		NCO-10		NCO-15	
	Discharge Time s	Specific Capacitance F/g	Discharge Time s	Specific Capacitance F/g	Discharge Time s	Specific Capacitance F/g
10	22	440	27.8	556	21.4	428
15	14.1	423	17.9	537	13.4	402
20	10.4	416	13	520	9.7	388
30	6.5	390	8.1	486	6	360

The NCO-10 electrode exhibits the highest specific capacitance at a definite current density compared to that of the other two electrodes, as seen in Table 3.2. For instance, the specific capacitances of NCO-5, NCO-10, and NCO-15 are calculated as 440, 556, and 428 F/g at 10 A/g, respectively. The specific capacitance values of the NCO-5 and NCO-10 electrodes are found to be similar to each other. Although the layer of NCO-5 electrode is the thinnest one, this is not the only factor to possess better electrochemical performance. Consequently, the NCO-10 nanosheets were chosen for the further enhancement experiment-reduced graphene oxide effects on electrochemical performance due to its captivating performance.

3.3.2.1. Cyclic performance

Cyclic performance is another vital subject for the supercapacitor applications. Therefore, the capacity retention of the NCO-10 electrode which has the highest specific capacitance than NCO-5 and NCO-15, was determined with the help of GCD measurement at a given discharge current density of 10 A/g after 3000 cycles (Figure 3.12). It is obvious that the specific capacitance firstly increases up to the 400th cycle. However, the specific capacitance starts to decrease as the charge/discharge cycle test continues. Such behavior can be described with the electro-activation mechanism originated from the wettability improvement of the electrode surface by the electrolyte in the progress of time. After 3000

cycles, the NCO-10 electrode retains 89% of its specific capacitance, indicating that the NCO-10 electrode is considered as a promising material for supercapacitors.

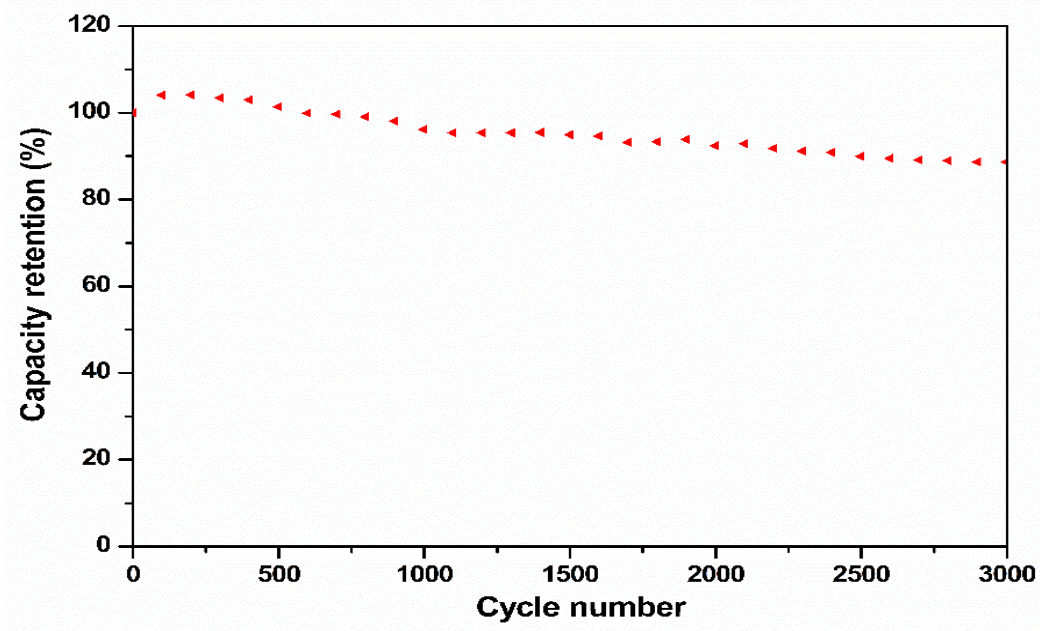


Figure 3.12. Cycling stability of NCO-10 electrode tested at of 10 A/g.

3.3.3. Electrochemical impedance spectroscopy (EIS) analyses

The capacitive qualification of as-fabricated nanosheets can be also investigated with the EIS analysis. The results of these tests are given in the form of the Nyquist diagram in Figure 3.13. It is seen that a depressed semicircle and a straight long line are detected at the high-frequency region and low-frequency region, respectively. In the Nyquist diagram, intrinsic impedance due to the resistances both electrode material and electrolyte (R_s), charge transfer resistance (R_{ct}), and ion diffusion impedance at the interface of electrolyte and electrode material (Z_w) are important parameters to evaluate the electrochemical performance. R_s was designated from the intercept of the Nyquist plot with the real axis at the high-frequency region and the results of R_s of NCO-5, NCO-10, and NCO-15 electrodes are 1.27, 1.25 and 1.30 ohms, respectively. The semicircle at the high-frequency region is related with to R_{ct} . As seen in this figure, although the semicircle diameters of all electrodes are similar, the slope of the NCO-10 electrode is closest to the Z'' axis at a low frequency which demonstrates its high capacitive performance and a small diffusion impedance of ions. Thus, the results confirm that the NCO-10 possesses

the highest specific capacitance as compared to that of two other electrodes due to its superior conductivity.

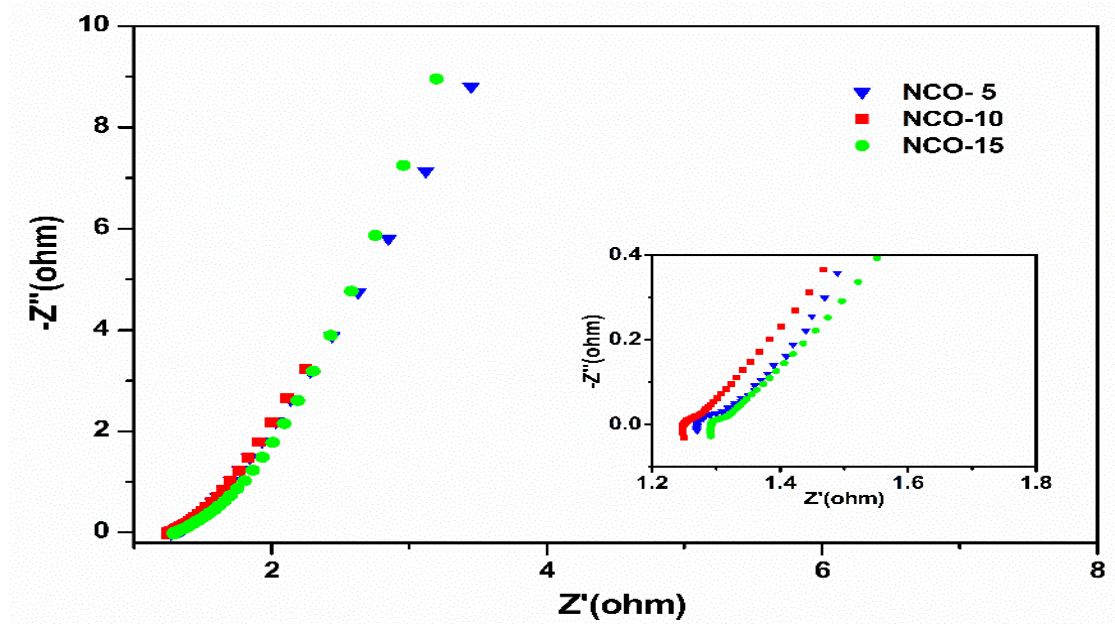


Figure 3.13. EIS (Nyquist) spectra of nanosheets in the frequency of 0.01-10⁵ Hz.

3.4. Enhancement of Performance of NCO with RGO

It is already recognized that in the case of usage of RGO as a carbon- based material with the pseudocapacitive material, a hybrid supercapacitor type can be successfully fabricated. The hybrid supercapacitor is better at providing higher specific capacitance but and especially admirable long cycling durability as compared to the other types of supercapacitor. Therefore, in this thesis, a new preparation method was conducted for the production of NCO-RGO hybrid supercapacitor. NCO-RGO hybrid- type supercapacitor was essentially fabricated by using the simultaneous electrodeposition of NCO and RGO in one stage. A composite of NCO and RGO was electrodeposited on the electrode surface with the first CV cycle and the amount of the film on the electrode surface increases with the following CV cycles. The amount of RGO in the NCO-RGO nanosheets was optimized by changing the amount of GO in the electrolyte solution and three different hybrids namely NCO(1:1)-10-rGO-0.10, NCO(1:1)-10-rGO-0.25, and NCO(1:1)-rGO-0.50 was prepared by 0.10 mg/mL, 0.25 mg/mL and 0.50 mg/mL GO respectively. After

that, the electrochemical features of these electrodes were evaluated with the CV, GCD, and EIS analyses.

3.5. Electrochemical Behaviors of NCO-RGO Electrodes

3.5.1. Cyclic voltammetry (CV) analyses

CV analyses were accomplished at diverse sweep rates varying between 5 to 50 mV/s in a given voltage range of -0.1-0.5 V vs. SCE by using a traditional three-electrode system in the presence of 2 M KOH. The results due to the CV measurements of NCO(1:1)-10-rGO-0.10, NCO(1:1)-10-rGO-0.25, and NCO(1:1)-10-rGO-0.50 electrodes present in the Figure 3.14.

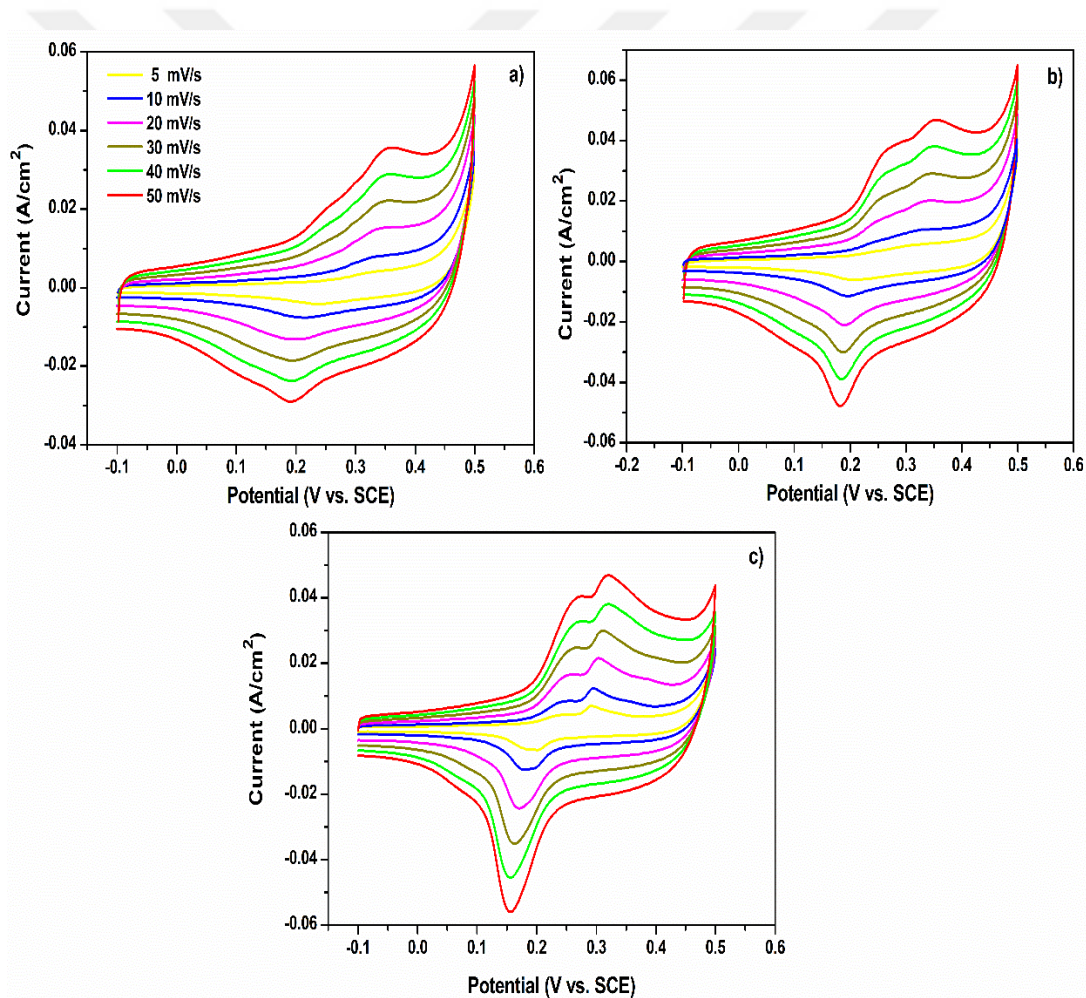


Figure 3.14. CV profiles of as-prepared nanosheets at various scan rates a) NCO(1:1)-10-rGO-0.1; b) NCO(1:1)-10-rGO-0.25; c) NCO(1:1)-10-rGO-0.50.

As seen in the Figure 3.14, a new oxidation new is detected before the wave of NCO originated from the oxidation of RGO in conjunction with NCO electrodeposition on Ni foam by adding GO in the electrolyte solution. Thus, the anodic peak is divided in two pairs obviously discovered between 0.20 and 0.40 V due to the redox reaction of RGO and NCO. The cathodic peak is detected at about 0.20 V. Furthermore, the redox couplers reversibility of NCO(1:1)-10-rGO-0.25 electrode does not remarkably change depend on the increase in scan rate, implying the fast charge/discharge mechanism of the pseudocapacitive material because of the low resistance of the prepared electrodes which is confirmed with the EIS measurement (Figure 3.19). A comparison of CV profiles of as-fabricated electrodes at 20 mV/s is also given in represented Figure 3.15. It is obvious that the peak current increases with the increment of graphene oxide amount in the electrolyte medium, resulting in higher specific capacitance determined under the area of CV curves.

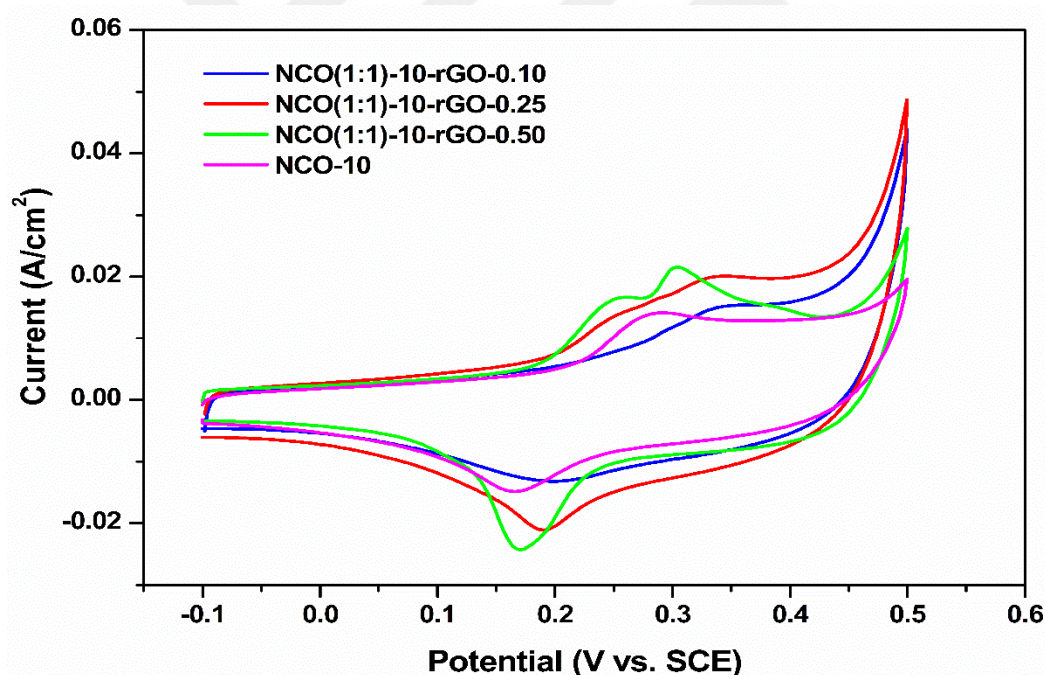


Figure 3.15. Comparison of CV profiles of the fabricated nanosheets at 20 mV/s.

3.5.2. Galvanostatic charge/discharge (GCD) analyses

GCD measurements were employed to find out the effect of RGO on the capacitive performance of as-prepared nanosheets. Therefore, GCD tests were done between the

potential window of 0-0.5 V vs. SCE at different current densities. The GCD experiments were also performed at diverse current densities in order to compare the capacitive performance of the nanosheets and the achieved charge/discharge curves are shown in Figure 3.16.

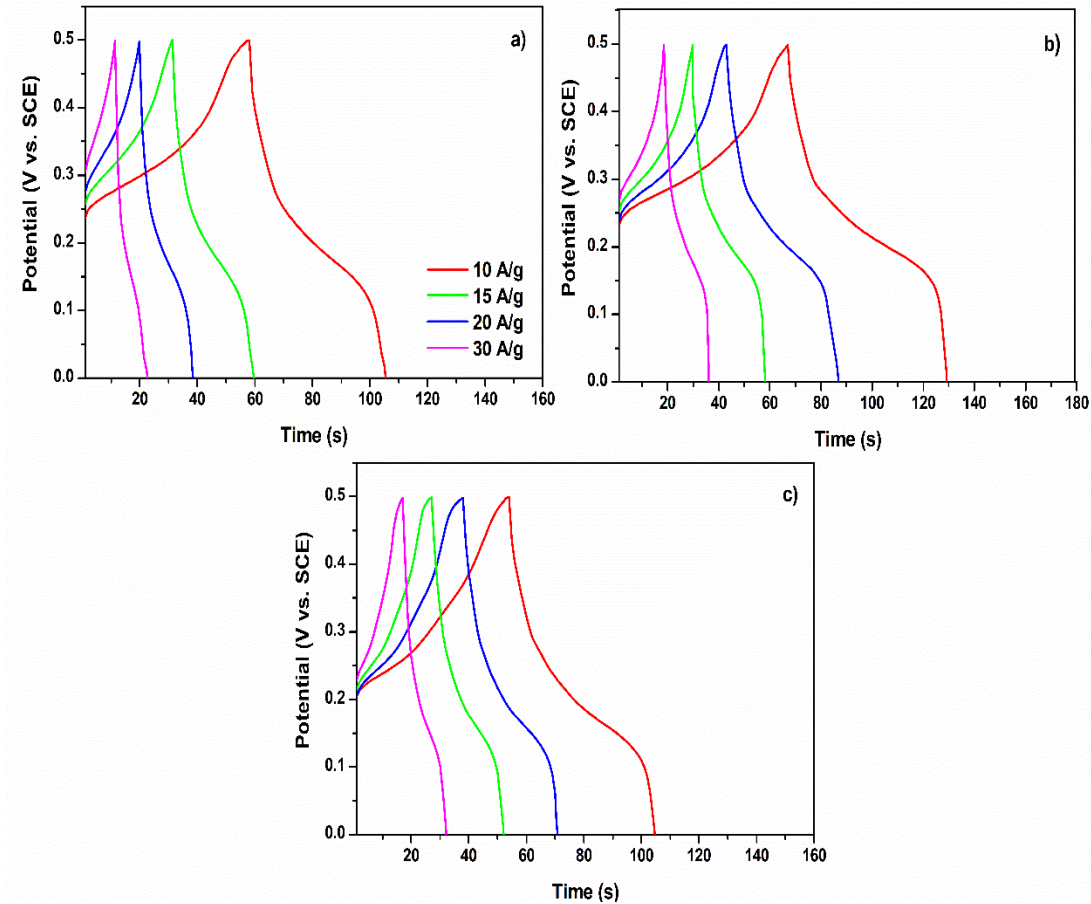


Figure 3.16. GCD profiles of the NCO-RGO nanosheets according to variable current density a) NCO(1:1)-10-rGO-0.10; b) NCO(1:1)-10-rGO-0.25; c) NCO(1:1)-10-rGO-0.50.

The specific capacitances of the electrodes were determined from the Equation (3.1). According to this equation, the specific capacitance of NCO(1:1)-10-rGO-0.10, NCO(1:1)-10-rGO-0.25, and NCO(1:1)-rGO-0.50 electrodes are calculated as 920, 1254.8 and 996 F/g at 10 A/g, respectively. As it is clear that NCO(1:1)-10-rGO-0.25 hybrid nanosheets provide the highest specific capacitance which is quite compatible with the CV measurement. In addition, the specific capacitance of NCO(1:1)-10-rGO-0.25 electrode is two-fold higher as compared with the NCO-10 electrode, indicating the

attractive effect of RGO on the performance. The calculated specific capacitances of NCO-RGO electrodes at various current densities are given in Table 3.3.

Table 3.3. The determined specific capacitances of electrodes electrodeposited simultaneously with reduced graphene oxide at diverse current densities.

Discharge Current Density A/g	NCO(1:1)-10-rGO-0.10		NCO(1:1)-10-rGO-0.25		NCO(1:1)-10-rGO-0.50	
	Discharge Time s	Specific Capacitance F/g	Discharge Time s	Specific Capacitance F/g	Discharge Time s	Specific Capacitance F/g
10	46	920.0	62.7	1254.8	49.8	996.0
15	28.4	852.0	40.7	1221.0	32.3	969.0
20	20.5	820.0	28.4	1136.0	24	960.0
30	12.9	774.0	18.2	1092.0	15	900.0

The electrochemical features of NCO(1:1)-10-rGO-0.25 hybrid nanosheets, which exhibited the highest specific capacitance determined by the optimization of reduced graphene oxide amount, were broadly studied to reveal the capacitive performance in utilization of supercapacitors. Therefore, the galvanostatic charge/discharge analyses were also examined at diverse discharge current densities changing from 1 to 30 A/g. The studies were performed up to charge potential of 0.45 V at low current densities. On the other hand, the charge potential for the fabricated electrode could be reached to 0.5 V at high current densities.

The GCD curves of NCO(1:1)-10-rGO-0.25 electrode changes approximately in linear which indicates high rate capability owing to the low internal charge transfer resistance, as seen in Figure 3.17. This experience is also a good agreement with the high Columbic efficiency given in Figure 3.18. The NCO(1:1)-10-rGO-0.25 electrode derives a high specific capacitance of 1655.8, 1557.3, 1491.1, 1411.1, 1254.8, 1221, 1136 and 1092 F/g at the current density of 1, 2, 3, 5, 10, 15, 20 and 30 A/g, respectively. In accordance with these results, the specific capacitance decreases depend on the increment of discharge current density. Such behavior can be described with insufficient active material amount

taking part in the oxidation/reduction reactions at high current densities owing to the fast ion transportation. The specific capacitance decreased to 1092 F/g in case of the current density of 30 A/g, demonstrating an impressive rate capability of 65.9% determined based on the specific capacitance at 1 A/g.

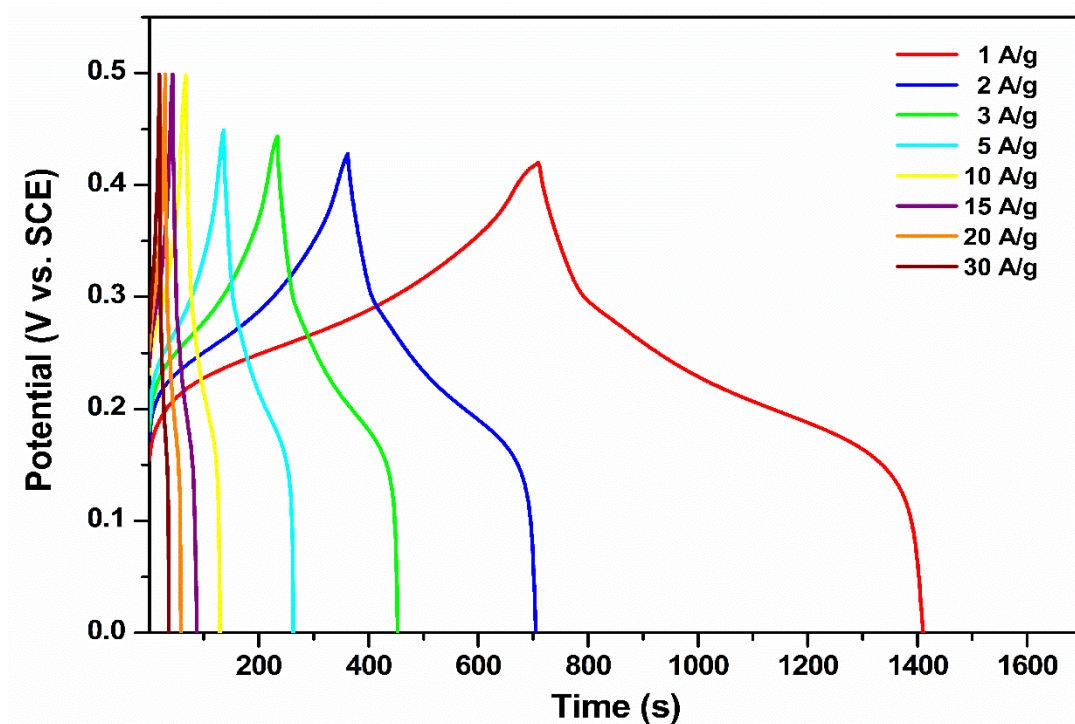


Figure 3.17. GCD curves of NCO(1:1)-10-rGO-0.25 nanosheets at various discharge current densities changing from 1 to 30 A/g.

3.5.2.1. Cyclic performance

The long cycling stability of NCO(1:1)-10-rGO-0.25 hybrid electrode was investigated by using charge/discharge measurement at the constant discharge current density of 10 A/g for 3000 cycles. As seen in Figure 3.18, the recognized behavior of NCO(1:1)-10-rGO-0.25 nanosheets involving reduced graphene oxide belongs to the stability curve is rather similar to the pure NCO nanosheets. The wetting capability of the basic solution on the electrode surface is improved due to the increase in immersion time. The ions diffusion rate further increases in time, progressively. Thus, the activation of NCO(1:1)-10-rGO-0.25 electrode enhances which is supported by the EIS measurements before and after the cycling performance experiment.

Even though the observed behavior is similar, the cycling stability of NCO(1:1)-10-rGO-0.25 hybrid electrode is successfully enhanced originated from the synergistic effect of reduced graphene oxide. After 3000 cycles, the remaining capacity is still 97.5% which is the best cycling performance among the similar Ni-Co based works previously reported. As a result, due to contributing RGO as a carbonous material in the structure of electrode by using the fabrication technique explained here, the lifespan of the prepared electrode is prolonged which provides advantages for practical applications of this electrode as a supercapacitor.

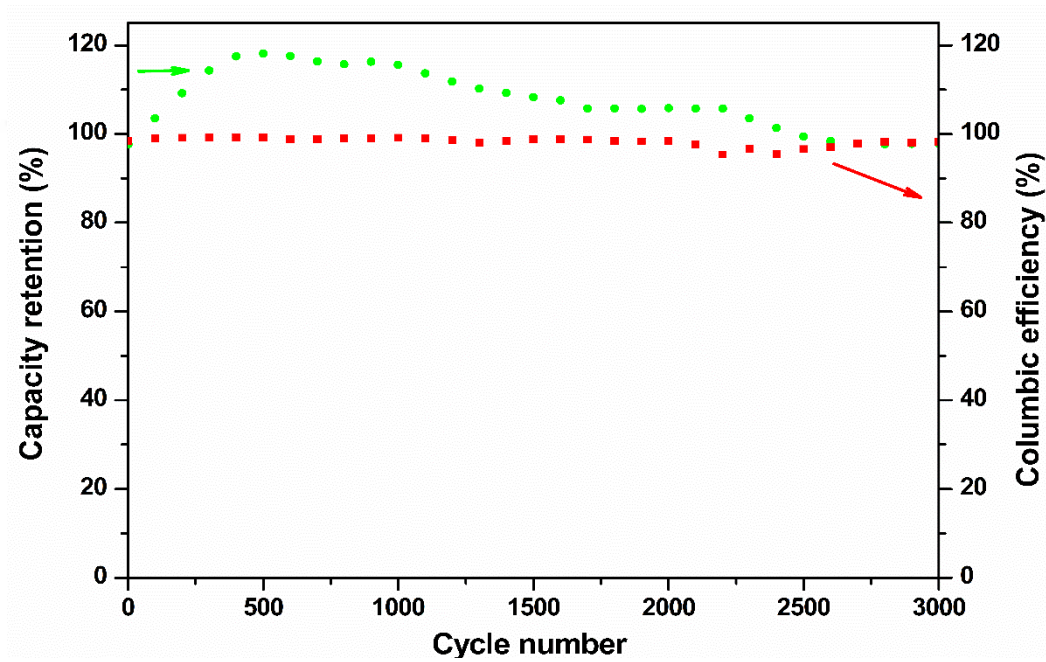


Figure 3.18. Cycling stability performance of NCO(1:1)-10-rGO-0.25 hybrid electrode carried out at the discharge current of 10 A/g.

3.5.3. Electrochemical impedance spectroscopy (EIS) analyses

The EIS analyses were also conducted to figure out the electrochemical properties of the NCO-RGO hybrid nanosheets and given in the form of Nyquist plots in Figure 3.19. As seen, all as-achieved spectra are comprised of a quasi-semicircle at the high-frequency area and a linear straight line at the low-frequency area. It is clear that with the addition of RGO in the networks, the internal resistance values of hybrid electrodes apparently decrease which is strong evidence for higher conductivity. The internal resistance (R_s) magnitudes were determined to be 0.82, 0.69 and 0.86 ohms for NCO(1:1)-10-rGO-0.10,

NCO(1:1)-10-rGO-0.25 and NCO(1:1)-10-rGO-0.50, respectively. These internal resistances are highly lower than the pure NCO-10 electrode. Furthermore, NCO-10-rGO-0.25 electrode has the lowest internal resistance among those of three electrodes. A significant development on the conductivity of NCO(1:1)-10-rGO-0.25 hybrid electrode due to the reduced graphene oxide contribution helps to provide higher capacitive performance depending upon the occurrence of a fast charge/discharge mechanism. Correlatively, NCO(1:1)-10-rGO-0.25 hybrid electrode has the lowest charge transfer resistance determined from the semicircle radius. As seen in Figure 3.19, the smallest semicircle is related to the NCO(1:1)-10-rGO-0.25 hybrid electrode.

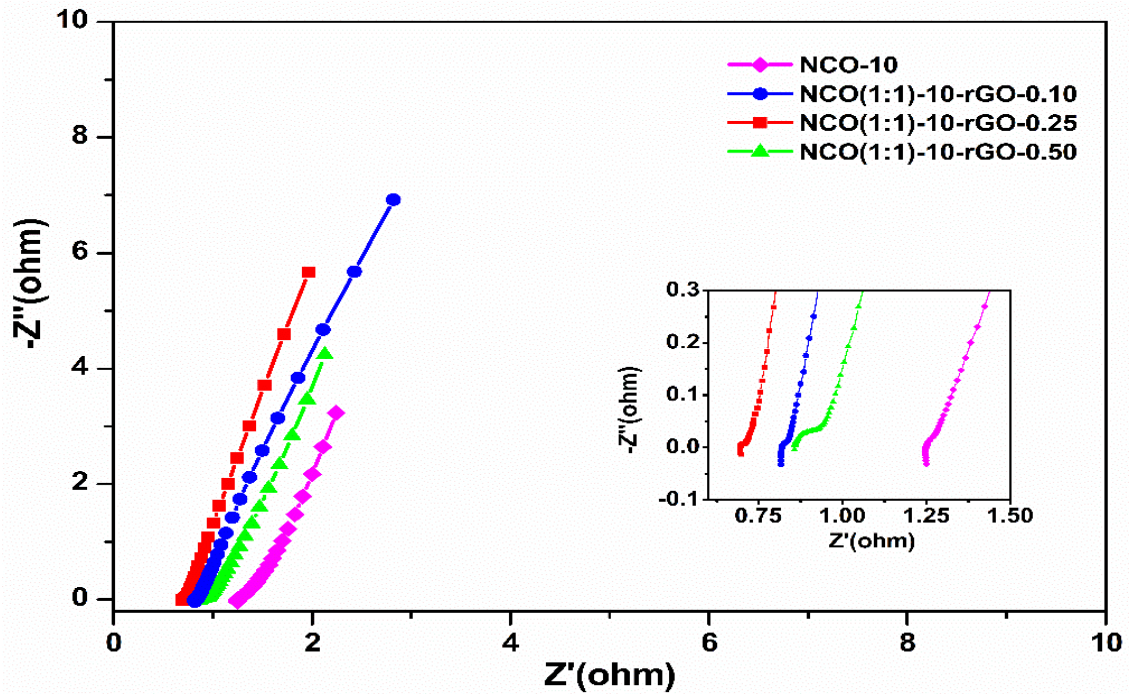


Figure 3.19. The EIS spectra of as-fabricated samples in Nyquist form.

Additionally, the EIS measurement of the NCO(1:1)-10-rGO-0.25 hybrid electrode was performed before and after the cycling stability experiment respectively, to evaluate its attractive electrochemical performance and the results are given as Nyquist plots (Figure 3.20). The R_s values of NCO(1:1)-10-rGO-0.25 hybrid electrode before and after the repetitive cycling test was found 0.69 and 0.39 ohms, respectively. After the mentioned test, it is obvious that the decrease of internal resistance helps to improve the ion diffusion and rate of electrolyte ions on the electrode surface, providing an effective progress on the electrochemical performance.

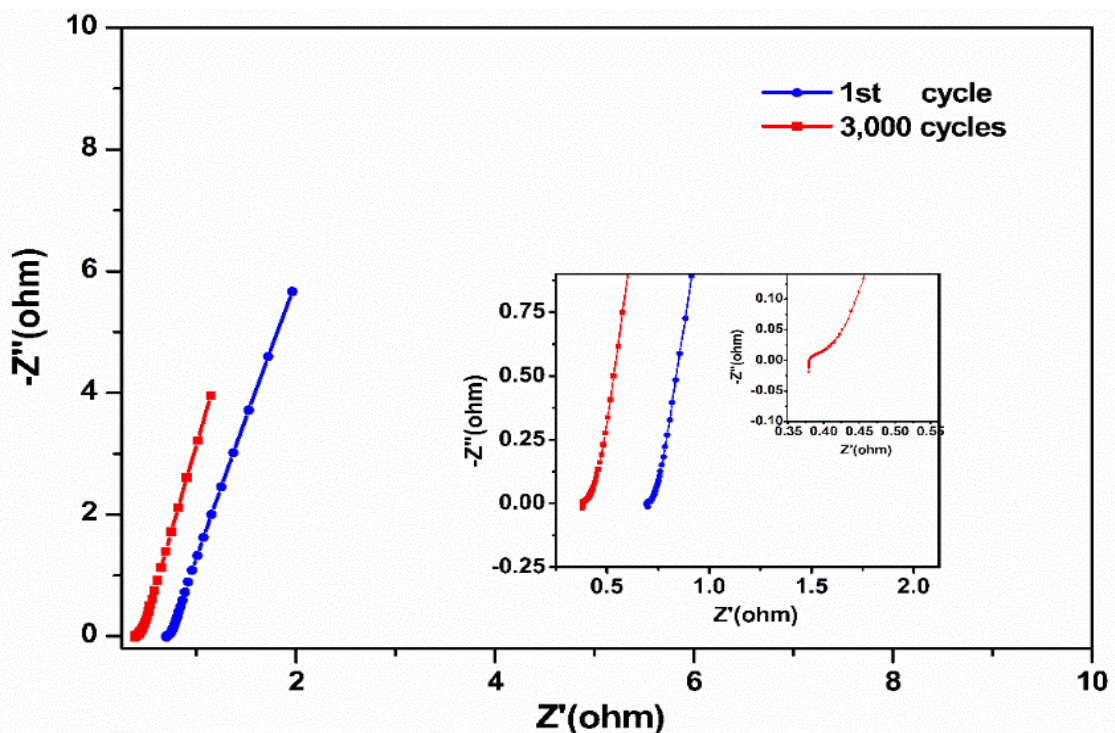


Figure 3.20. The Nyquist plots of NCO(1:1)-10-rGO-0.25 hybrid electrode before and after the cycling stability tests, respectively.

3.6. The Effect of Ni-Co Ratio in the Electrolyte Solution

The content of Ni and Co components directly changes the structure and morphology as well as electrochemical performance reported previous works. Therefore, in this section, the effect of various Ni-Co molar ratio in the electrolyte was comprehensively studied. To explore the appropriate conditions, NCO-RGO hybrid electrodes in six different Ni-Co molar ratio solutions were prepared. All electrolyte solutions also involved 0.25 mg/mL graphene oxide which was determined as an optimum value in previous section. The diverse films due to NCO and RGO simultaneously electrodeposition in different electrolytes composed of different Ni-Co molar ratio by CV method were fabricated on the electrode surface. After that, to explore their probability as electrode material for supercapacitors, electrochemical measurements such as CV, GCD, and EIS were examined in detail.

3.7. Electrochemical Performance of NCO(x:y)-RGO Electrodes

3.7.1. Cyclic voltammetry (CV) analyses

CV tests were carried out at diverse scan rates changing from 5 to 50 mV/s in the voltage range of -0.1-0.5 V vs. SCE. The CV profiles of as-fabricated electrodes are given in Figure 3.21. It is distinctly seen that the behaviors of all CV curves are reversible which is an evidence of the Faradic mechanism originated from the oxidation and reduction reactions. Subsequently, all the CV profiles of the as-achieved nanosheets at different ratios display immensely symmetric redox peaks, suggesting their good reversibility. Furthermore, it is obvious that the peak currents increase with related to the increase in scan rate because of the fast ions diffusion.

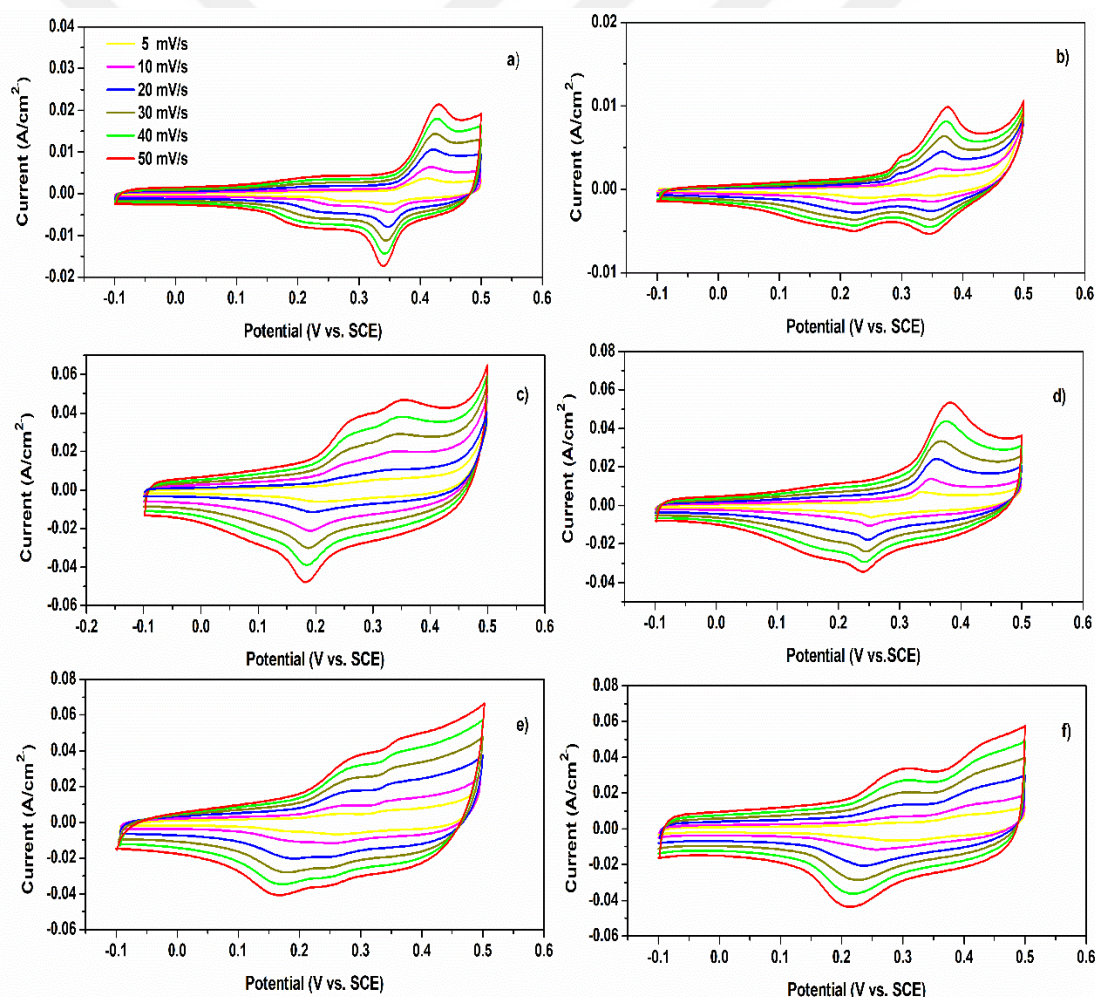


Figure 3.21. The CV profiles of prepared NCO-RGO hybrids at various current densities a) NCO(1:0)-10-rGO-0.25; b) NCO(0:1)-10-rGO-0.25; c) NCO(1:1)-10-rGO-0.25; d) NCO(1:2)-10-rGO-0.25; e) NCO(2:1)-10-rGO-0.25; f) NCO(4:1)-10-rGO-0.25.

The changes in the redox peaks in accordance with the content of Ni or Co component at a scan rate of 20 mV/s are shown in Figure 3.22. As seen, the redox peaks of binary metal oxides are broader as compared to a single form, indicating the advantage of the binary system on the electrochemical performance derived from the contribution of both metal ions. With the combination of Ni and Co ions in the electrolyte, the positions of cathodic peaks shift to more negative potentials, implying a relatively low resistance of the electrode which helps to develop the performance. In addition, with the increasing of Co molar ratio in the electrolyte, the anodic peaks apparently shift to more negative potentials. Therefore, the addition of Co causes to reduce in the specific capacitance, and thus, the NCO(1:2)-10-rGO-0.25 hybrid with a high Co content further exhibits a comparatively low specific capacitance. This observation is in good agreement with the previously reported works [18, 92]. Additionally, it can be found that the area surrounded by the cyclic voltammetry curve of the NCO(2:1)-10-rGO-0.25 electrode is greater as compared to those of other electrodes, demonstrating the highest specific capacitance.

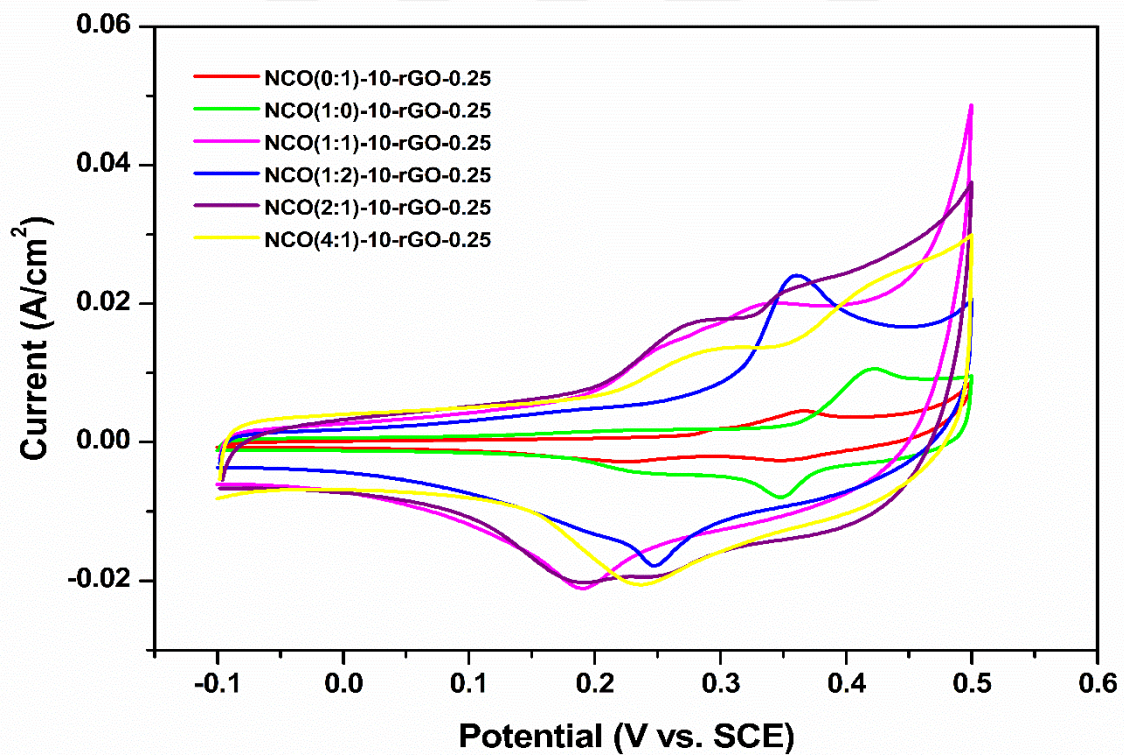


Figure 3.22. The CV profiles of the all NCO-RGO hybrids at 20 mV/s.

3.7.2. Galvanostatic charge/discharge (GCD) analyses

GCD analyses were studied to determine the effect of different Ni and Co ratios in the fabricated samples on the electrochemical performance. Hence, GCD measurements were performed at various current densities under the same conditions mentioned previous analyses. The results of GCD experiments at different current densities are given in Figure 3.23 to compare the capacitive performance of the hybrid electrodes. In compatible with the CV measurements, the shape of the GCD curves essentially displays a pseudocapacitive behavior which can be ascribed to the Faradic reactions originated from the active material on the electrode surface. As can be also observed in the insert of Figure 3.23, the GCD curves of NCO-RGO samples are still symmetric with respect to the increase in current densities, implying that these materials have better stability due to the combination of Ni and Co components in the electrode structure. On the other hand, the curve shapes of NCO(1:0)-10-rGO-0.25 and NCO(0:1)-10-rGO-0.25 electrodes are not to be similar to each other. Additionally, it is clear that the NCO(2:1)-10-rGO-0.25 electrode has the longest discharge time which means to the highest specific capacitance. The specific capacitances of as-prepared electrodes at different current densities are calculated by using the Equation (3.1) and the results are presented in Table 3.4.

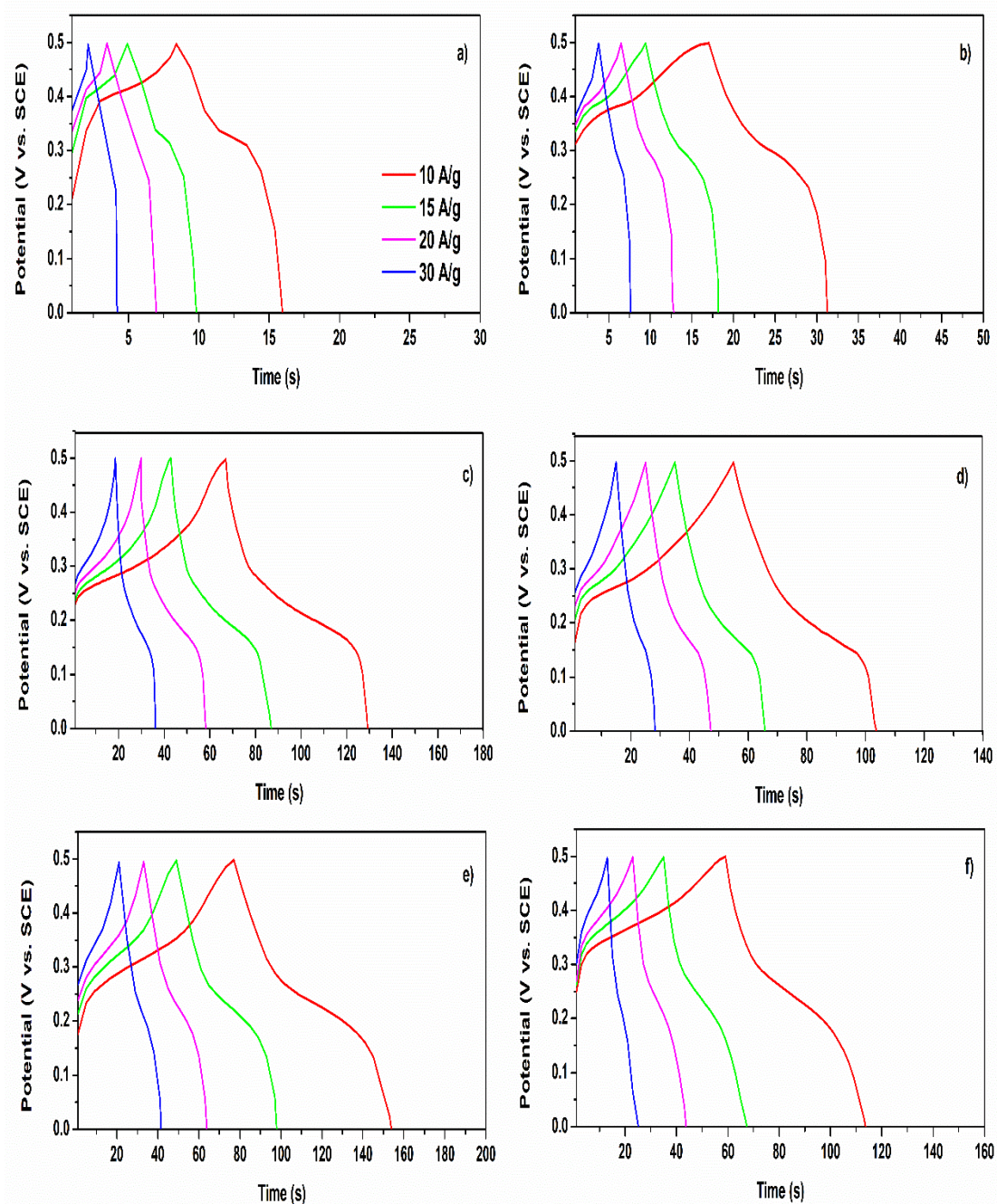


Figure 3.23. The GCD profiles of fabricated NCO-RGO hybrids at diverse current densities a) NCO(0:1)-10-rGO-0.25; b) NCO(1:0)-10-rGO-0.25; c) NCO(1:1)-10-rGO-0.25; d) NCO(1:2)-10-rGO-0.25; e) NCO(2:1)-10-rGO-0.25; f) NCO(4:1)-10-rGO-0.25.

Table 3.4. The specific capacitances of as-prepared hybrid electrodes at different current densities.

Discharge Current Density A/g	NCO(1:0)-10-rGO-0.25		NCO(0:1)-10-rGO-0.25		NCO(1:1)-10-rGO-0.25	
	Discharge Time s	Specific Capacitance F/g	Discharge Time s	Specific Capacitance F/g	Discharge Time s	Specific Capacitance F/g
10	14.3	286.0	7.6	152.0	62.7	1254.8
15	8.7	261.0	4.9	147.0	40.7	1221.0
20	6.13	245.2	3.5	140.0	28.4	1136.0
30	3.7	222.0	2.12	127.2	18.2	1092.0
Discharge Current Density A/g	NCO(1:2)-10-rGO-0.25		NCO(2:1)-10-rGO-0.25		NCO(4:1)-10-rGO-0.25	
	Discharge Time s	Specific Capacitance F/g	Discharge Time s	Specific Capacitance F/g	Discharge Time s	Specific Capacitance F/g
10	46.9	938.0	73.8	1476.0	55.2	1104.0
15	30.1	903.0	45.9	1377.0	34.1	1023.0
20	22.1	884.0	31.5	1260.0	21.8	872.0
30	13.9	834.0	19.8	1188.0	13.5	810.0

As given in Table 3.4, the NCO(2:1)-10-rGO-0.25 electrode exhibits the best performance at all studied current densities as compared to those of other electrodes. Thus, to get more information about the capacitive performance of NCO(2:1)-10-rGO-0.25 nanosheets, the GCD experiments were further conducted at lower current densities. The limit of charge potential was up to 0.45 V and 0.5 V at low current densities and high current densities, respectively, similar to Section 3.5.2. The GCD profiles of NCO(2:1)-10-rGO-0.25 electrode does not change depending on the current density, demonstrating the admirable rate capability because of the low charge transfer resistance (Figure 3.24). The NCO(2:1)-10-rGO-0.25 electrode exhibits high specific capacitance of 1916.5, 1843.6, 1733.3, 1666.7, 1476, 1377, 1260 and 1188 F/g at the current density of 1, 2, 3,

5, 10, 15, 20 and 30 A/g, respectively. The specific capacitance reduces in response to the increasing in current density which can be ascribed to the fast ion transfer at high current densities. The specific capacitance remains 1188 F/g at 30 A/g, indicating a remarkable rate capability of 62% calculated according to the specific capacitance at 1 A/g.

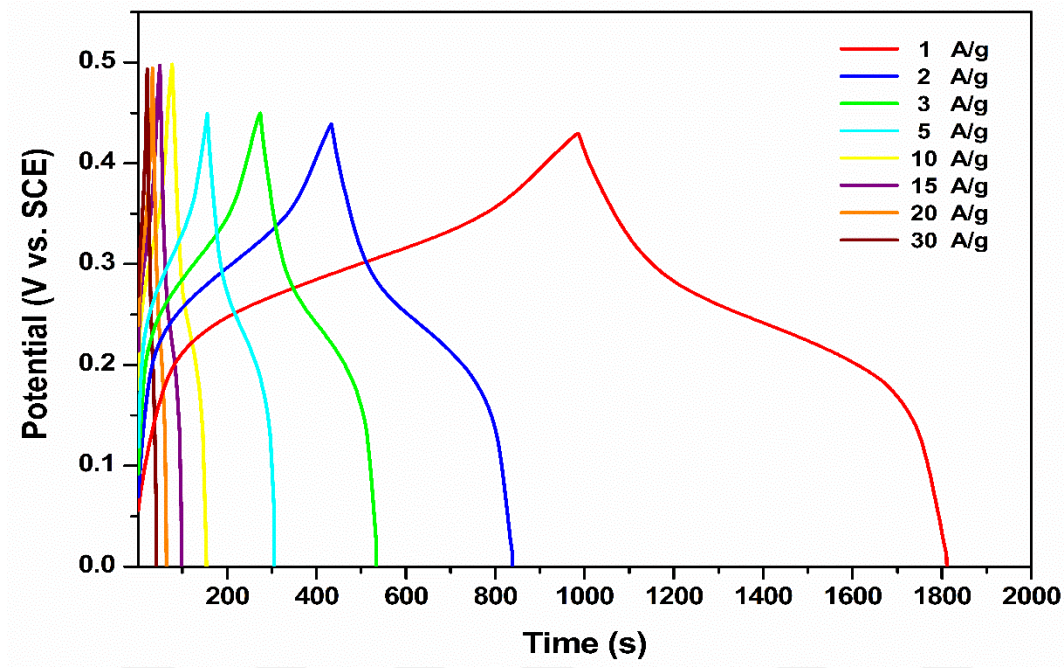


Figure 3.24. The GCD curves of the NCO(2:1)-10-rGO-0.25 nanosheet depending on the variable current densities.

3.7.2.1. Cyclic performance

The long term cycling performances of NCO-RGO hybrid electrodes prepared with different Ni and Co content were examined with the help of the GCD approach at 10 A/g for continuous 3000 cycles and the results are supplied in Figure 3.25. The observed behaviors of all samples are similar to each other except the NCO(1:2)-10-rGO-0.25 with higher Co contents which is more stable among the other electrodes. Such behavior can be described as improved electrical conductivity due to the increasing Co amount in the electrode structure which is supported by the results of EIS measurement (Figure 3.26). On the other hand, the capacitive performance of samples with higher Ni content increases at first, and then decreases with cycling numbers. Such behavior can be ascribed to the enhancement in the surface wettability of the electrode as the charge/discharge

cycles continue, resulting in more electroactive surface areas [94]. After the entire 3000 cycles, the NCO(1:1)-10-rGO-0.25, NCO(1:2)-10-rGO-0.25, NCO(2:1)-10-rGO-0.25 and NCO(4:1)-10-rGO-0.25 electrodes still retain the capacity of 97.5%, 95.6%, 98.1% and 93.8%, respectively which implies an attractive long term stability at high current density. In conclusion, these gained capacity values after cycling tests are higher compared to the pure NCO nanosheets which demonstrates the remarkable effect of the RGO in the structure.

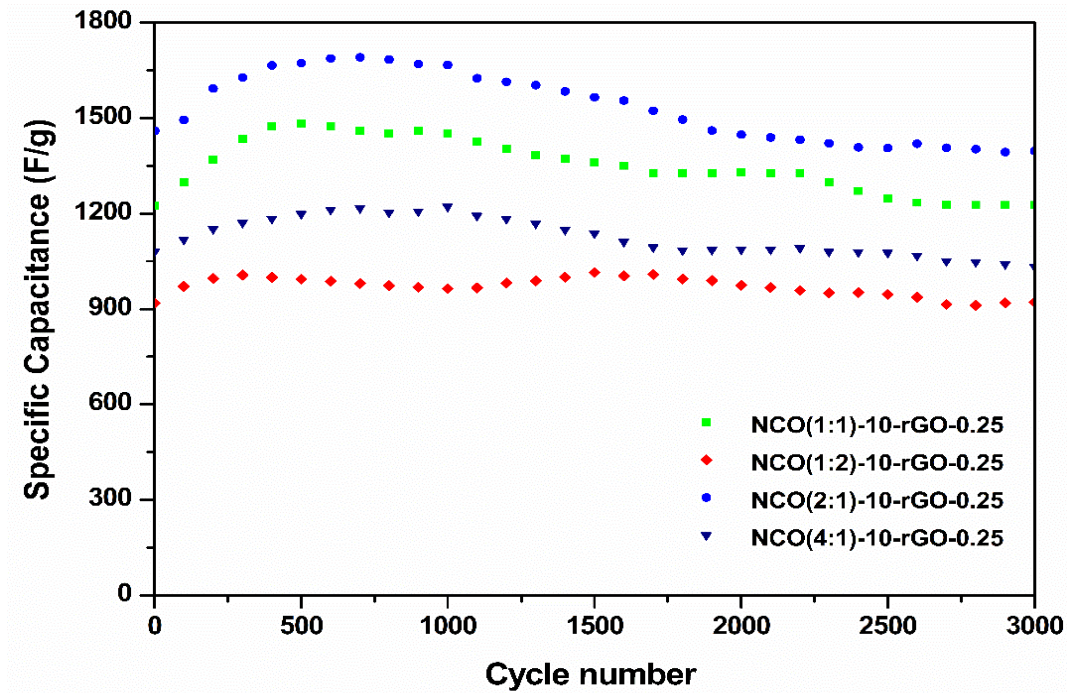


Figure 3.25. Long term stability results of the NCO-RGO hybrid electrodes conducted at a discharge current of 10 A/g.

3.7.3. Electrochemical impedance spectroscopy (EIS) analyses

The all Nyquist plots of the nanosheets presented in Figure 3.26. display similar shape in consideration of the previous examined electrodes. The R_s of NCO(2:1)-10-rGO-0.25, NCO(1:1)-10-rGO-0.25, NCO(4:1)-10-rGO-0.25 and NCO(1:2)-10-rGO-0.25 are estimated as 0.51, 0.69, 0.72 and 0.72 ohms, respectively. Thus, it can be decided that R_s decreases with the increase of the Ni content in the electrode structure, showing the decrease in the internal resistance. Furthermore, as seen, increasing Co content in the structure the slope of curves in the low-frequency zone becomes closer to the straight line

which can be explained with the enhanced conductivity of the as-fabricated electrodes due to the contribution of Co component. In line with these observations, the curve of NCO(2:1)-10-rGO-0.25 in the low- frequency region is almost vertical line which is related to the improved capacitive performance due to the rapid ion diffusion capability. On the other hand, the charge transfer resistance (R_{ct}) of NCO(2:1)-10-rGO-0.25 electrode represented as the semicircle at the high-frequency region is relatively lower than among the other electrodes which related to the higher specific capacitance. Therefore, The Nyquist plots indicate that the NCO(2:1)-10-rGO-0.25 electrode has the lowest impedances compared to those of other electrodes.

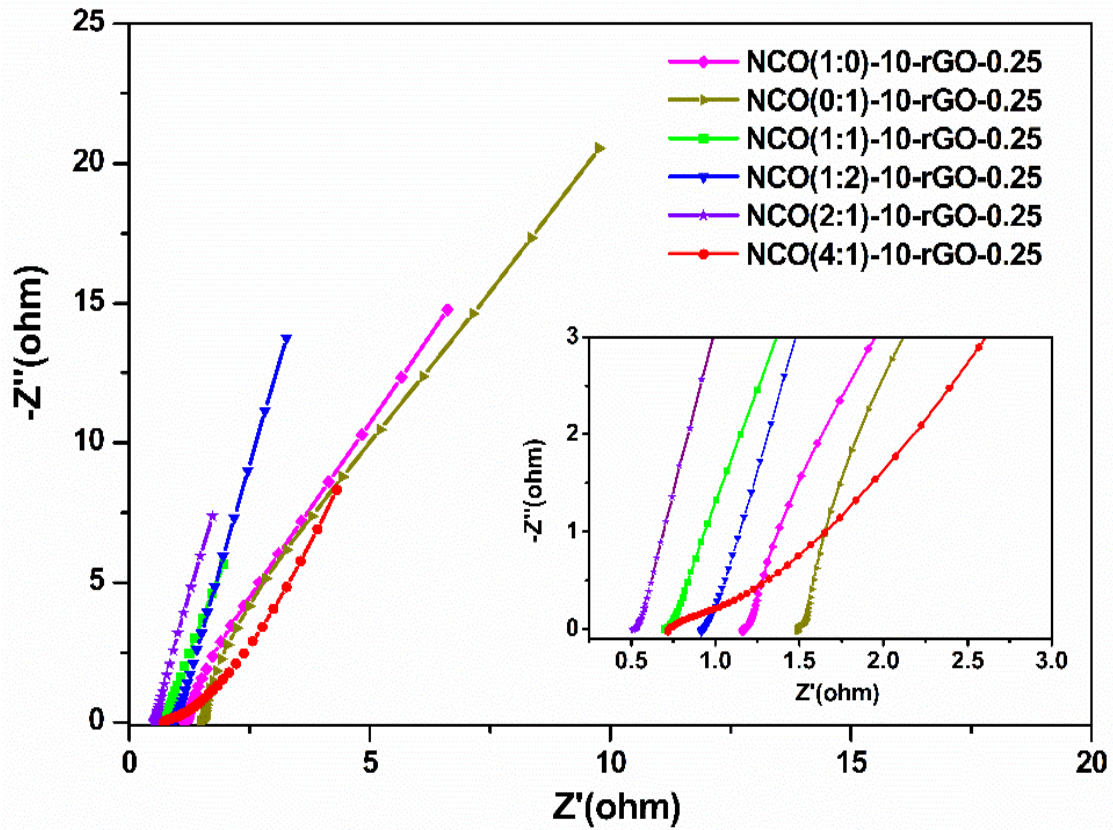


Figure 3.26. The Nyquist plots of as-prepared hybrid electrodes between the frequency of $0.01-10^5$ Hz.

In addition, to investigate the capacitive performance of the NCO(2:1)-10-rGO-0.25 hybrid electrode, EIS analyses were conducted before and after the long term stability test, respectively and the spectra in the Nyquist forms are given in Figure 3.27. It is clear that after the cycling test, the R_s reduces from 0.51 ohm to 0.35 ohm, indicating the promoted ion transfer rate between the active material and the electrolyte after stability

analysis. The semicircle of the NCO(2:1)-10-rGO-0.25 electrode after the aforementioned test becomes smaller resulting from an increase in conductivity because of the enhanced wettability of the electrolyte on the electrode surface in time. Both of the results can confirm that the improved electrochemical properties of NCO(2:1)-10-rGO-0.25 electrode help to derive the highest capacitive performance.

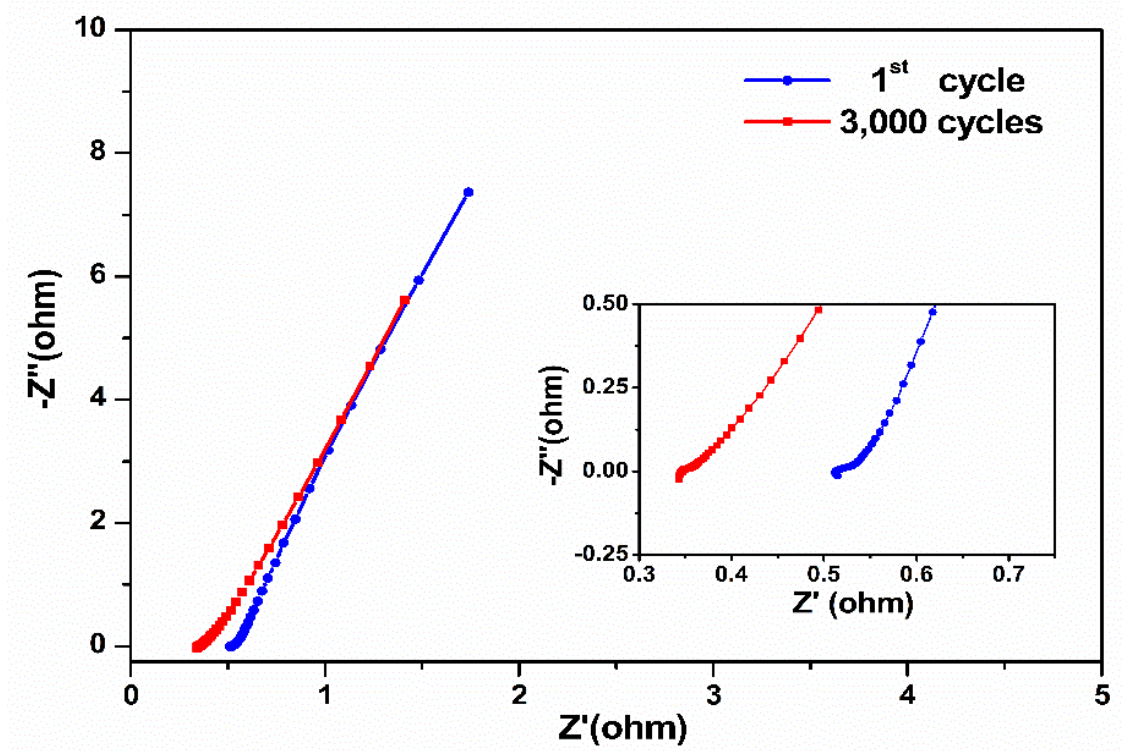


Figure 3.27. The EIS spectra of Nyquist plots of NCO(2:1)-10-rGO-0.25 hybrid electrode before and after the cycling stability tests, respectively.

Table 3.5 fundamentally represents the comparison of performance between the present work and several Ni-Co based supercapacitors reported in the literature. In this study, we fabricated the NCO-RGO hybrid structure by applying one step and simultaneous electrodeposition of NCO and RGO with the cyclic voltammetry technique which significantly improves the basic electrochemical performances, particularly the specific capacitance and lifespan, compared to the related studies in the literature.

Table 3.5. The performance comparison of supercapacitor electrodes with similar structures from previous literature to present work.

Material	Method	Specific Capacitance	Retention	Ref.
NiCo ₂ O ₄	Electrodeposition	1012.5 F/g at 3 A/g	85.6% 2500 cycle at 20 A/g	[16]
NiCo ₂ O ₄	Solvothermal	440 F/g at 5 mV/s	94% 2000 cycle at 8 A/g	[89]
NiCo ₂ O ₄	Solvothermal	122.5 C/g at 1 A/g	78% 6000 cycle at 2 A/g	[93]
NiCo ₂ O ₄	Sol-gel method	1254 F/g at 2 A/g	70.4% 1000 cycle at 2 A/g	[94]
NiCo ₂ O ₄ /rGO	Hydrothermal	1003 F/g at 1 A/g	57% 10000 cycle at 10 A/g	[103]
Ni-Co LDH	Electrodeposition	1540 F/g at 1 A/g	82.9% 5000 cycle at 10 A/g	[86]
Hierarchical Ni-Co LDH	Electrodeposition	1454.2 F/g at 1 A/g	73.5% 5000 cycle at 10 A/g	[102]
NiCo ₂ O ₄ @MnO ₂	Electrodeposition	913.6 F/g at 0.5 A/g	87.1% 3000 cycle at 16 A/g	[104]
Co/Ni LDH	Electrodeposition	1587.5 F/g at 0.5A/g	91.5% 1000 cycle at 5 A/g	[17]
(NCH)/graphene (G)	Electrodeposition	1410 F/g at 2 A/g	94.2% 2500 cycle at 4 A/g	[92]
NiCo ₂ S ₄ (NCS)-CS	Hydrothermal	1093 F/g at 0.5 A/g	83% 8000 cycle at 8 A/g	[105]
NCO(2:1)-10-rGO-0.25	One step Electrodeposition	1916.5 F/g at 1 A/g	95.6 % 3000 cycle at 10 A/g	this work

3.8. The Energy Density and Power Density

The energy density and power density of the electrodes are further critical factors to estimate the electrochemical performance of supercapacitors. Thus, the energy and the power density were estimated by using the equation (3.2) and (3.3) [17]

$$E = C_s \times (\Delta V)^2 / 7.2 \quad (3.2)$$

$$P = 3600 \times E / \Delta t \quad (3.3)$$

where E represents the energy density in form of Wh/kg, P states the power density (W/kg), C_s depicts the specific capacitance of (F/g), ΔV is the potential difference (V), and Δt describes the discharge time (s).

The NCO(2:1)-10-rGO-0.25 hybrid electrode exhibits the highest energy density of 53.90 Wh/kg at a power density of 235.5 W/kg and the energy density remains a considerably high value of 41.2 Wh/kg at 7500 W/kg. The energy density performance of the NCO(2:1)-10-rGO-0.25 hybrid is also higher than those of previously reported Ni-Co based electrodes at the similar preparation technique (~ 22.6 Wh/kg at ~ 5.4 kW/kg [9], ~ 32.2 Wh/kg at ~ 4 kW/kg [106], and ~ 24 Wh/kg at ~ 0.2 kW/kg [87]). Such a comparison demonstrates that the fabricated NCO(2:1)-10-rGO-0.25 nanosheets enables to achieve a better performance for being utilized as an electrode for supercapacitor applications.



4. CONCLUSIONS

In this study, a novel technique, one-step electrodeposition has been simultaneously performed for the fabrication of electrodes composed of nickel cobalt oxide and reduced graphene oxide. Firstly, the NCO structure was synthesized on Ni-foam and found out the optimum coating layer depends on the electrochemical performance. Secondly, the NCO nanosheets were modified with RGO and its effects were investigated, resulting to designate the optimum value. At the end of this work, the NCO-RGO nanosheets were prepared from the electrolyte solution including different Ni-Co molar ratio to achieve the best performance.

The XRD measurements were done for the characterization of the structures of as-fabricated materials. However, there was no characteristic peak derived from the Ni-Co metal oxides or RGO detected in the XRD spectra due to the obtained films having very low thickness. XPS analysis was studied to identify the surface composition and the oxidation states of the elements of as-fabricated materials. The typical survey spectra indicated that the hybrid electrode was composed of Ni, Co, O, and RGO, supporting the results obtained from EDS measurement. Raman measurements were conducted to examine the vibrational and morphological characteristics of the electrodes both NCO and NCO-RGO. The detected peaks at Raman spectra approved that the electrodeposition and reduction of NCO and GO simultaneously occurred. The observed shifts in the peak positions also resulted from the doping effect of RGO in the electrode structure. SEM analysis was performed to elaborate on the size and morphology of the NCO and NCO-RGO materials. The SEM images proved the existence of ultrathin RGO layers coated on the surface of substrate. Furthermore, the results indicated that with the content of RGO, the surface morphology became more porous network structure with numerous large open spaces and electroactive surface sites which leads to increase the electrochemical performance. The electrode of NCO-RGO had vertically standing wrinkled nanosheets with a thickness of approximately 25-60 nm. EDS measurement was accomplished to observe the atomic compositions of the NCO(2:1)-10-rGO-0.25 electrode. The obtained result verified the presence of Ni, Co, O, and C components in the structure of the related electrode.

Pseudocapacitive activity experiments were accomplished by using the cyclic voltammetry technique. All results confirmed that the as-prepared electrodes of NCO exhibited redox-active characteristics depend on approximately uniform CV peaks at diverse scan rates which demonstrates their strong pseudo-capacitive performance owing to the Faradic reactions. On the other hand, pseudocapacitive performance was investigated with the GCD tests at different discharge current densities. The optimum electrodeposition coating layer was found out 10 according to specific capacitance values (NCO-10). The achieved specific capacitance at 10 A/g was 556 F/g and the capacitance was preserved 89% at 10 A/g at the end of 3000 charge/discharge cycles. In addition, the accuracy of the performance electrode at 10 layers was supported with the EIS analysis which provides insight about the conductivity.

After the optimization of coating layers, the reduced graphene oxide as a carbonous material was aimed to combine to the structure of NCO to improve the specific capacitance and especially to provide remarkable long cycling stability. The NCO-RGO electrodes also had redox couplers with excellent reversibility at different scan rates, indicating their fast charge/discharge mechanism due to the low resistance of the obtained electrodes which was proved with the EIS measurements. The GCD analyses were performed to determine the effect of reduced graphene oxide on the electrochemical performance. The NCO(1:1)-10-rGO-0.25 electrode displayed the highest specific capacitance fabricated from including 0.25 mg/mL GO in the electrolyte solution. The obtained specific capacitance was estimated to be 1254.8 F/g which was two-folded higher compared to the NCO-10 electrode. The electrochemical performance was further investigated at low current densities to reveal the capacitive performance as a binder-free electrode for supercapacitors and the specific capacitance was achieved 1655.8 F/g at 1 A/g with the enhanced cycling performance of 97.5% at 10 A/g after 3000 charging/discharging.

Furthermore, the effect of various Ni-Co ratio (1:0, 0:1, 1:1, 2:1, 1:2, 4:1) in the electrolyte solution involving 0.25 mg/mL GO (the optimum value) was comprehensively studied. The GCD curves of NCO-RGO materials were symmetric concerning the increase in discharge current densities, suggesting that these materials have better stability because of the combination of Ni and Co components in the electrode structure. The results indicated that the increase in the content of Ni in the structure leads to development

in the specific capacitance. The NCO(2:1)-10-rGO-0.25 electrode possessed the longest discharge time meaning to the highest specific capacitance of 1476 F/g at 10 A/g compared to others while it had 1916.5 F/g at 1 A/g which is higher most of previously reported works mentioned in Table 3.5. According to the EIS measurements, the internal resistances (R_s) of NCO(2:1)-10-rGO-0.25, NCO(1:1)-10-rGO-0.25, NCO(4:1)-10-rGO-0.25 and NCO(1:2)-10-rGO-0.25 were estimated quite low as 0.51, 0.69, 0.72 and 0.72 ohms, respectively, indicating their significantly high conductivity. Hence, it was noticeable that R_s reduced with the increase of the Ni content in the electrode structure which supports the GCD measurements. Additionally, RGO enhanced to the lifespan of the electrodes confirmed from the cycling stability analysis and NCO(2:1)-10-rGO-0.25 electrode retain its 95.6% of specific performance at the end of 3000 cycles at a high current density of 10 A/g. Besides, the NCO(2:1)-10-rGO-0.25 hybrid electrode displayed the highest energy density of 53.90 Wh/kg at a power density of 235.5 W/kg and the energy density remains an appreciably high value of 41.2 Wh/kg at 7500 W/kg.

In conclusion, it can be stated that the NCO electrode modified with the RGO exhibited attractive electrochemical performance. Thus, this study provides a new platform for transition metal oxides with enhanced electrochemical performance in utilization as promising facile, binder-free electrode material for next-generation supercapacitor applications.

REFERENCES

1. Sahoo, S., Naik, K.K., Rout, C.S. (2015) Electrodeposition of spinel MnCo(2)O(4) nanosheets for supercapacitor applications. *Nanotechnology*, 26(45),455401.
2. Sahoo, S., Mondal, R., Late, D.J., Rout, C.S. (2017) Electrodeposited Nickel Cobalt Manganese based mixed sulfide nanosheets for high performance supercapacitor application. *Microporous and Mesoporous Materials*, 244,101-108.
3. Wang, Y., Wang, L., Wei, B., Miao, Q., Yuan, Y., Yang, Z., Fei, W. (2015) Electrodeposited nickel cobalt sulfide nanosheet arrays on 3D-graphene/Ni foam for high-performance supercapacitors. *RSC Advances*, 5(121),100106-100113.
4. Vignesh, V., Subramani, K., Sathish, M., Navamathavan, R. (2018) Electrochemical investigation of manganese ferrites prepared via a facile synthesis route for supercapacitor applications. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 538,668-677.
5. Shinde, S.K., Ramesh, S., Bathula, C., Ghodake, G.S., Kim, D.Y., Jagadale, A.D., Kadam, A.A., Waghmode, D.P., Sreekanth, T.V.M., Kim, H.S., Nagajyothi, P.C., Yadav, H.M. (2019) Novel approach to synthesize NiCo₂S₄ composite for high-performance supercapacitor application with different molar ratio of Ni and Co. *Sci Rep*, 9(1),13717.
6. Xu, S., Su, C., Wang, T., Ma, Y., Hu, J., Hu, J., Hu, N., Su, Y., Zhang, Y., Yang, Z. (2018) One-step electrodeposition of nickel cobalt sulfide nanosheets on Ni nanowire film for hybrid supercapacitor. *Electrochimica Acta*, 259,617-625.
7. Jadhav, S., Kalubarme, R.S., Terashima, C., Kale, B.B., Godbole, V., Fujishima, A., Gosavi, S.W. (2019) Manganese dioxide/ reduced graphene oxide composite an electrode material for high-performance solid state supercapacitor. *Electrochimica Acta*, 299,34-44.
8. Xu, J., Sun, Y., Lu, M., Wang, L., Zhang, J., Tao, E., Qian, J., Liu, X. (2018) Fabrication of the porous MnCo₂O₄ nanorod arrays on Ni foam as an advanced electrode for asymmetric supercapacitors. *Acta Materialia*, 152,162-174.
9. Shahrokhian, S., Rahimi, S., Mohammadi, R. (2018) Nickel-cobalt layered double hydroxide ultrathin nanosheets coated on reduced graphene oxide

- nonosheets/nickel foam for high performance asymmetric supercapacitors. *International Journal of Hydrogen Energy*, 43(4),2256-2267.
10. Mirzaee, M.,Dehghanian, C. (2018) Pulsed electrodeposition of reduced graphene oxide on Ni NiO foam electrode for high-performance supercapacitor. *International Journal of Hydrogen Energy*, 43(27),12233-12250.
 11. Akyüz, D., Keskin, B., Şahintürk, U., Koca, A. (2016) Electrocatalytic hydrogen evolution reaction on reduced graphene oxide electrode decorated with cobaltphthalocyanine. *Applied Catalysis B: Environmental*, 188,217-226.
 12. Ke, Q.,Wang, J. (2016) Graphene-based materials for supercapacitor electrodes – A review. *Journal of Materiomics*, 2(1),37-54.
 13. Beka, L.G., Li, X., Liu, W. (2017) Nickel Cobalt Sulfide core/shell structure on 3D Graphene for supercapacitor application. *Sci Rep*, 7(1),2105.
 14. Kim, Y., Cho, E.-s., Park, S.-J., Kim, S. (2016) One-pot microwave-assisted synthesis of reduced graphene oxide/nickel cobalt double hydroxide composites and their electrochemical behavior. *Journal of Industrial and Engineering Chemistry*, 33,108-114.
 15. Chebrolu, V.T., Balakrishnan, B., Raman, V., Cho, I., Bak, J.-S., Prabakar, K., Kim, H.-J. (2020) Co-electrodeposition of NiCu(OH)₂@Ni-Cu-Se hierarchical nanoparticle structure for supercapacitor application with enhanced performance. *Applied Surface Science*, 506.
 16. Wang, W., Li, Z., Meng, A., Li, Q. (2018) Network-like holey NiCo₂O₄ nanosheet arrays on Ni foam synthesized by electrodeposition for high-performance supercapacitors. *Journal of Solid State Electrochemistry*, 23(2),635-644.
 17. Wei, M., Huang, Q., Zhou, Y., Peng, Z., Chu, W. (2018) Ultrathin nanosheets of cobalt-nickel hydroxides hetero-structure via electrodeposition and precursor adjustment with excellent performance for supercapacitor. *Journal of Energy Chemistry*, 27(2),591-599.
 18. Xing, J., Wu, S., Ng, K.Y.S. (2015) Electrodeposition of ultrathin nickel–cobalt double hydroxide nanosheets on nickel foam as high-performance supercapacitor electrodes. *RSC Advances*, 5(108),88780-88786.

19. Yuksel, İ., Kaygusuz, K. (2011) Renewable energy sources for clean and sustainable energy policies in Turkey. *Renewable and Sustainable Energy Reviews*, 15, 4132–4144.
20. Aneke, M., Wang, M. (2016) Energy storage technologies and real life applications – A state of the art review. *Applied Energy*, 179, 350-377.
21. Akinyele, D.O., Rayud, R.K. (2014) Review of energy storage technologies for sustainable power networks. *Sustainable Energy Technologies and Assessments*, 8, 74–91.
22. Yang, Y., Bremner, S., Menictas, C., Kay, M. (2018) Battery energy storage system size determination in renewable energy systems: A review. *Renewable and Sustainable Energy Reviews*, 91, 109-125.
23. Raza, W., Ali, F., Raza, N., Luo, Y., Kim, K.-H., Yang, J., Kumar, S., Mehmood, A., Kwon, E.E. (2018) Recent advancements in supercapacitor technology. *Nano Energy*, 52, 441-473.
24. Xia, L., Yu, L., Hu, D., Chen, G.Z. (2017) Electrolytes for electrochemical energy storage. *Materials Chemistry Frontiers*, 1(4), 584-618.
25. Zhou, Z., Benbouzid, M., Charpentier, J.F., Scullier, F., Tang, T. (2013) A review of energy storage technologies for marine current energy systems. *Renewable and Sustainable Energy Reviews*, 18, 390–400.
26. Gallo, A.B., Simões-Moreira, J.R., Costa, H.K.M., Santos, M.M., Moutinho dos Santos, E. (2016) Energy storage in the energy transition context: A technology review. *Renewable and Sustainable Energy Reviews*, 65, 800-822.
27. Koohi-Fayegh, S., Rosen, M.A. (2020) A review of energy storage types, applications and recent developments. *Journal of Energy Storage*, 27.
28. Chen, H., Cong, T.N., Yang, W., Tan, C., Li, Y., Ding, Y. (2009). Progress in electrical energy storage system: A critical review. *Progress in Natural Science* 19, 291–312.
29. Nazir, H., Batool, M., Bolivar Osorio, F.J., Isaza-Ruiz, M., Xu, X., Vignarooban, K., Phelan, P., Inamuddin, Kannan, A.M. (2019) Recent developments in phase change materials for energy storage applications: A review. *International Journal of Heat and Mass Transfer*, 129, 491-523.

30. Rajeshwar, K., Baltruschat, H., Sun, Y.K. (2014) Electrochemical Energy Conversion: Past, Present, and Future. *Chemphyschem*.
31. Chen, K.,Xue, D. (2016) Materials chemistry toward electrochemical energy storage. *Journal of Materials Chemistry A*, 4(20),7522-7537.
32. Zhang, L., Hu, X., Wang, Z., Sun, F., Dorrell, D.G. (2018) A review of supercapacitor modeling, estimation, and applications: A control/management perspective. *Renewable and Sustainable Energy Reviews*, 81,1868-1878.
33. Poonam, Sharma, K., Arora, A., Tripathi, S.K. (2019) Review of supercapacitors: Materials and devices. *Journal of Energy Storage*, 21,801-825.
34. Kuperman, A.,Aharon, I. (2011) Battery–ultracapacitor hybrids for pulsed current loads: A review. *Renewable and Sustainable Energy Reviews*, 15(2),981-992.
35. Afif, A., Rahman, S.M.H., Tasfiah Azad, A., Zaini, J., Islan, M.A., Azad, A.K. (2019) Advanced materials and technologies for hybrid supercapacitors for energy storage – A review. *Journal of Energy Storage*, 25.
36. González, A., Goikolea, E., Barrena, J.A., Mysyk, R. (2016) Review on supercapacitors: Technologies and materials. *Renewable and Sustainable Energy Reviews*, 58,1189-1206.
37. Lin, M.C., Gong, M., Lu, B., Wu, Y., Wang, D.Y., Guan, M., Angell, M., Chen, C., Yang, J., Hwang, B.J., Dai, H. (2015) An ultrafast rechargeable aluminium-ion battery. *Nature*, 520(7547),325-8.
38. Deng, D. (2015) Li-ion batteries: basics, progress, and challenges. *Energy Science & Engineering*, 3(5),385-418.
39. Shobana, M.K. (2019) Metal oxide coated cathode materials for Li ion batteries – A review. *Journal of Alloys and Compounds*, 802,477-487.
40. Pelletier, S., Jabali, O., Laporte, G., Veneroni, M. (2017) Battery degradation and behaviour for electric vehicles: Review and numerical analyses of several models. *Transportation Research Part B: Methodological*, 103,158-187.
41. Zhao, B., Ran, R., Liu, M., Shao, Z. (2015) A comprehensive review of Li₄Ti₅O₁₂-based electrodes for lithium-ion batteries: The latest advancements and future perspectives. *Materials Science and Engineering: R: Reports*, 98,1-71.

42. Chen, A., Sen, P.K. (2016) Advancement in Battery Technology: A State-of-the-Art Review. 2016 IEEE Industry Applications Society Annual Meeting Industry Applications Society Annual Meeting, 2016 IEEE. :1-10 Oct, 2016, Portland.
43. Han, X., Lu, L., Zheng, Y., Feng, X., Li, Z., Li, J., Ouyang, M. (2019) A review on the key issues of the lithium ion battery degradation among the whole life cycle. *eTransportation*, 1.
44. Chan, K.-Y., Jia, B., Lin, H., Hameed, N., Lee, J.-H., Lau, K.-T. (2018) A critical review on multifunctional composites as structural capacitors for energy storage. *Composite Structures*, 188,126-142.
45. Sharma, P., Bhatti, T.S. (2010) A review on electrochemical double-layer capacitors. *Energy Conversion and Management*, 51(12),2901-2912.
46. Chung, D.D.L. (2018) Development, design and applications of structural capacitors. *Applied Energy*, 231,89-101.
47. Low, W.H., Khiew, P.S., Lim, S.S., Siong, C.W., Ezeigwe, E.R. (2019) Recent development of mixed transition metal oxide and graphene/mixed transition metal oxide based hybrid nanostructures for advanced supercapacitors. *Journal of Alloys and Compounds*, 775,1324-1356.
48. Fic, K., Platek, A., Piwek, J., Frackowiak, E. (2018) Sustainable materials for electrochemical capacitors. *Materials Today*, 21(4),437-454.
49. Libich, J., Máca, J., Vondrák, J., Čech, O., Sedlářiková, M. (2018) Supercapacitors: Properties and applications. *Journal of Energy Storage*, 17,224-227.
50. Muzaffar, A., Ahamed, M.B., Deshmukh, K., Thirumalai, J. (2019) A review on recent advances in hybrid supercapacitors: Design, fabrication and applications. *Renewable and Sustainable Energy Reviews*, 101,123-145.
51. Vangari, M., Pryor, T., Jiang, L. (2013) Supercapacitors: Review of Materials and Fabrication Methods. *Journal of Energy Engineering*, 139(2),72-79.
52. Javed, K., Ashfaq, H., Singh, R. (2019) Application of Supercapacitor as Hybrid Energy Storage Device in Stand-alone PV System. *International Conference on Power Electronics, Control and Automation (ICPECA) Power Electronics, Control and Automation (ICPECA)*, 2019 International Conference on. :1-4 Nov, 2019, New Delhi.

53. Zhao, J., Tian, Y., Liu, A., Song, L., Zhao, Z. (2019) The NiO electrode materials in electrochemical capacitor: A review. *Materials Science in Semiconductor Processing*, 96,78-90.
54. Stevica, Z., Vujasinovica, M.R., Bugarinovicb S., Dekanski, A. (2010) Construction and Characterisation of Double Layer Capacitors. *ACTA PHYSICA POLONICA A*, 117, 228-233.
55. Daniela C. Marcano, D.V.K., † Jacob M. Berlin, Alexander Sinitskii, Zhengzong Sun,,Alexander Slesarev, L.B.A., Wei Lu, and James M. Tour (2010) Improved Synthesis of Graphene Oxide. *ACS Applied Nano Materials*, 4(8),4806-4814.
56. Singh, R.K., Kumar, R., Singh, D.P. (2016) Graphene oxide: strategies for synthesis, reduction and frontier applications. *RSC Adv.*,6, 64993-65011.
57. Li, F., Jiang, X., Zhao, J., Zhang, S. (2015) Graphene oxide:A promising nanomaterial for energy and environmental applications. *Nano Energy*, 16, 488–515.
58. Compton, O.C, Nguyen, S.T. (2010) Graphene Oxide, Highly Reduced Graphene Oxide, and Graphene: Versatile Building Blocks for Carbon-Based Materials. *Small Journal*, 6(6), 711–723.
59. Pei, S., Cheng, H. (2012) The reduction of graphene oxide. *Carbon*, 50, 3210 – 3228.
60. Mao, S., Pu, H., Chen, J. (2012) Graphene oxide and its reduction: modeling and experimental progress. *RSC Advances*, 2, 2643–2662.
61. Toh, S.Y., Loh, K.S., Kamarudin, S.K., Daud, W.R.W. (2014) Graphene production via electrochemical reduction of graphene oxide: Synthesis and characterisation. *Chemical Engineering Journal*, 251,422-434.
62. Zhang, Y., Feng, H., Wu, X., Wang, L., Zhang, A., Xia, T., Dong, H., Li, X., Zhang, L. (2009) Progress of electrochemical capacitor electrode materials: A review. *International Journal of Hydrogen Energy*, 34(11),4889-4899.
63. Yu, L.,Chen, G.Z. (2016) Redox electrode materials for supercapatteries. *Journal of Power Sources*, 326,604-612.
64. Lin, Z., Goikolea, E., Balducci, A., Naoi, K., Taberna, P.L., Salanne, M., Yushin, G., Simon, P. (2018) Materials for supercapacitors: When Li-ion battery power is not enough. *Materials Today*, 21(4),419-436.

65. Kouchachvili, L., Yaïci, W., Entchev, E. (2018) Hybrid battery/supercapacitor energy storage system for the electric vehicles. *Journal of Power Sources*, 374,237-248.
66. Sánchez-Jiménez, M., Estrany, F., Alemán, C. (2017) Improving the fabrication of all-polythiophene supercapacitors. *Polymer Science, Series B*, 59(2),194-201.
67. Liu, H., Liu, X., Wang, S., Liu, H.-K., Li, L. (2020) Transition metal based battery-type electrodes in hybrid supercapacitors: A review. *Energy Storage Materials*, 28,122-145.
68. Wang, D.-G., Liang, Z., Gao, S., Qu, C., Zou, R. (2020) Metal-organic framework-based materials for hybrid supercapacitor application. *Coordination Chemistry Reviews*, 404.
69. Zhong, C., Deng, Y., Hu, W., Qiao, J., Zhang, L., Zhang, J. (2015) A review of electrolyte materials and compositions for electrochemical supercapacitors. *Chem Soc Rev*, 44(21),7484-539.
70. Barzegar, F., Momodu, D. Y., Fashedemi, O.O., Bello, A., Dangbegnona, J.K., Manyala, N. (2015) Investigation of different aqueous electrolytes on the electrochemical performance of activated carbon-based supercapacitors. *RSC Advances*, 5, 107482-107487.
71. Ramachandran, R., Wang, F. (2018) Electrochemical Capacitor Performance: Influence of Aqueous Electrolytes. *Intechopen*, 51-68.
72. Wang, A., Li, Y., Lou, F., Melandsø Buan, M.E., Sheridanb, E., Chen, D. (2017) Enhancing capacitance of supercapacitor with both organic electrolyte and ionic liquid electrolyte on a biomass-derived carbon. *RSC Advances*, 7, 23859-23865.
73. Sangeun Cho a, S.L.a., Bo Hou b, Jongmin Kim a, Yongcheol Jo a, Hyeonseok Woo a, Sambhaji M. Pawar a, Akbar I. Inamdar a, Youngsin Park c, SeungNam Cha b, Hyungsang Kim a, **, Hyunsik Im (2018) Optimizing nanosheet nickel cobalt oxide as an anode material for bifunctional electrochemical energy storage and oxygen electrocatalysis. *Electrochimica Acta* 274,279-287.
74. Dhere, S. (2018) Electrode materials for supercapacitors synthesized by sol–gel process. *Current Science*, 115(3), 436-449.

75. Xua, P., Liua, J., Liua, T., Yea, K., Chenga, K., Yina, J., Caoa, D., Wang, G., Li, Q. (2013) Preparation of binder-free of CuO/Cu₂O/Cu composites: A novel electrode material for supercapacitor applications. *RSC Advances*, 00, 1-9.
76. Ingham, B., Toney, M.F., X-ray diffraction for characterizing metallic films, in *Metallic Films for Electronic, Optical and Magnetic Applications*. 2014. p. 3-38.
77. Lewandowska, R., Liu, J. (2016) Raman Microscopy: Analysis of Nanomaterials. *Reference Module in Materials Science and Materials Engineering*, 1-6.
78. Minati, L., Micheli, V., Ngoc Tran, L.T., Zur, L., Lukowiak, A., Chiasera, A., Ferrari, M., Speranza, G. (2019) XPS Characterization of Materials for Photonic Applications. *Photonics & Electromagnetics Research Symposium, Spring (PIERS | SPRING)*, Rome, 17-20 June, Italy.
79. Singh, A.K. (2016) Experimental Methodologies for the Characterization of Nanoparticles. *Engineered Nanoparticles*, 4, 125-170.
80. Chooto, P. (2019) *Cyclic Voltammetry and Its Applications*. Intechopen, 1-14.
81. Lee, S., Kim, J., Yoon, J. (2017) Preparation and application of urchin-like TiO₂/activated carbon for high performance hybrid supercapacitors. *Journal of Ceramic Processing Research*, 18(1), 51-54.
82. Wang, H., Xu, Z., Yi, H., Wei, H., Guo, Z., Wang, X. (2014) One-step preparation of single-crystalline Fe₂O₃ particles/graphene composite hydrogels as high performance anode materials for supercapacitors. *Nano Energy*, 7, 86–96.
83. Stoller, M.D., Ruoff, R.S. (2010) Best practice methods for determining an electrode material's performance for ultracapacitors. *Energy & Environmental Science*, 3(9).
84. Liu, X.Y., Gong, T.C., Zhang, J., Ji, J., Huo, W.C., Cao, T., Zhang, Y.X., Zhang, X., Liu, Y. (2019) Engineering hydrogenated manganese dioxide nanostructures for high-performance supercapacitors. *J Colloid Interface Sci*, 537, 661-670.
85. Randviir, E.P., Banks, C.E. (2013) Electrochemical impedance spectroscopy: an overview of bioanalytical applications. *Analytical Methods*, 5, 1098-1115..
86. Li, Y., Shan, L., Sui, Y., Qi, J., Wei, F., He, Y., Meng, Q., Ren, Y., Liu, J. (2019) Ultrathin Ni–Co LDH nanosheets grown on carbon fiber cloth via electrodeposition for high-performance supercapacitors. *Journal of Materials Science: Materials in Electronics*, 30(14), 13360-13371.

87. Mitchell, E., Jimenez, A., Gupta, R.K., Gupta, B.K., Ramasamy, K., Shahabuddin, M., Mishra, S.R. (2015) Ultrathin porous hierarchically textured NiCo₂O₄-graphene oxide flexible nanosheets for high-performance supercapacitors. *New Journal of Chemistry*, 39(3),2181-2187.
88. Zhou, J., Huang, Y., Cao, X., Ouyang, B., Sun, W., Tan, C., Zhang, Y., Ma, Q., Liang, S., Yan, Q., Zhang, H. (2015) Two-dimensional NiCo₂O₄ nanosheet-coated three-dimensional graphene networks for high-rate, long-cycle-life supercapacitors. *Nanoscale*, 7(16),7035-9.
89. Sethi, M.,Bhat, D.K. (2019) Facile solvothermal synthesis and high supercapacitor performance of NiCo₂O₄ nanorods. *Journal of Alloys and Compounds*, 781,1013-1020.
90. Xie, L., Li, K., Sun, G., Hu, Z., Lv, C., Wang, J., Zhang, C. (2012) Preparation and electrochemical performance of the layered cobalt oxide (Co₃O₄) as supercapacitor electrode material. *Journal of Solid State Electrochemistry*, 17(1),55-61.
91. Yang, M., Cheng, H., Gu, Y., Sun, Z., Hu, J., Cao, L., Lv, F., Li, M., Wang, W., Wang, Z., Wu, S., Liu, H., Lu, Z. (2015) Facile electrodeposition of 3D concentration-gradient Ni-Co hydroxide nanostructures on nickel foam as high performance electrodes for asymmetric supercapacitors. *Nano Research*, 8(8),2744-2754.
92. Bai, Y., Wang, W., Wang, R., Sun, J., Gao, L. (2015) Controllable synthesis of 3D binary nickel-cobalt hydroxide/graphene/nickel foam as a binder-free electrode for high-performance supercapacitors. *Journal of Materials Chemistry A*, 3(23),12530-12538.
93. Jiang, W., Hu, F., Yan, Q., Wu, X. (2017) Investigation on electrochemical behaviors of NiCo₂O₄ battery-type supercapacitor electrodes: the role of an aqueous electrolyte. *Inorganic Chemistry Frontiers*, 4(10),1642-1648.
94. Zhu, Y., Ji, X., Wu, Z., Song, W., Hou, H., Wu, Z., He, X., Chen, Q., Banks, C.E. (2014) Spinel NiCo₂O₄ for use as a high-performance supercapacitor electrode material: Understanding of its electrochemical properties. *Journal of Power Sources*, 267,888-900.

95. Li, M., Bo, X., Mu, Z., Zhang, Y., Guo, L. (2014) Electrodeposition of nickel oxide and platinum nanoparticles on electrochemically reduced graphene oxide film as a nonenzymatic glucose sensor. *Sensors and Actuators B: Chemical*, 192,261-268.
96. Vidotti, M., Salvador, R.P., Ponzio, E.A., Córdoba de Torresi, S.I. (2007) Mixed Ni/Co Hydroxide Nanoparticles Synthesized by Sonochemical Method. *Nanoscience and Nanotechnology*, 7, 3221–3226.
97. Sun, Y., Zhang, W., Li, D., Gao, L., Hou, C., Zhang, Y., Liu, Y. (2015) Facile synthesis of MnO₂/rGO/Ni composite foam with excellent pseudocapacitive behavior for supercapacitors. *Journal of Alloys and Compounds*, 649,579-584.
98. Jiang, W., Shen, L., Wang, K., Wang, Z., Tian, Z. (2019) Wear resistance of Ni-Co/SiC composite coating by jet electrodeposition in the presence of magnetic field. *Proceedings of the Institution of Mechanical Engineers, Part B: Journal of Engineering Manufacture*, 234(3),431-438.
99. Sangeun Cho a, S.L.a., Bo Hou b, Jongmin Kim a, Yongcheol Jo a, Hyeonseok Woo a, Sambhaji M. Pawar a, Akbar I. Inamdar a, Youngsin Park c, SeungNam Cha b, Hyungsang Kim a, **, Hyunsik Im (2018) Optimizing nanosheet nickel cobalt oxide as an anode material for bifunctional electrochemical energy storage and oxygen electrocatalysis. *Electrochimica Acta* 274,279 - 287.
100. Nguyen, V.H., Lamiel, C., Shim, J.-J. (2016) Mesoporous 3D graphene@NiCo₂O₄ arrays on nickel foam as electrodes for high-performance supercapacitors. *Materials Letters*, 170,105-109.
101. Tanışık, İ., Uğuz, Ö., Akyüz, D., Zunain Ayaz, R.N., Sarioğlu, C., Karaca, F., Özkaya, A.R., Koca, A. (2020) Solar-hydrogen production with reduced graphene oxide supported Cd_xZn_{1-x}S photocatalysts. *international journal of hydrogen energy*, xxx (x x x x) xxx.
102. Jiang, L., Sui, Y., Qi, J., Chang, Y., He, Y., Meng, Q., Wei, F., Sun, Z., Jin, Y. (2017) Hierarchical Ni-Co layered double hydroxide nanosheets on functionalized 3D-RGO films for high energy density asymmetric supercapacitor. *Applied Surface Science*, 426,148-159.

103. Zhang, S., Gao, H., Zhou, J., Jiang, F., Zhang, Z. (2019) Hydrothermal synthesis of reduced graphene oxide-modified NiCo₂O₄ nanowire arrays with enhanced reactivity for supercapacitors. *Journal of Alloys and Compounds*, 792,474-480.
104. Zhang, Y., Wang, B., Liu, F., Cheng, J., Zhang, X.-w., Zhang, L. (2016) Full synergistic contribution of electrodeposited three-dimensional NiCo₂O₄@MnO₂ nanosheet networks electrode for asymmetric supercapacitors. *Nano Energy*, 27,627-637.
105. Liang, X., Nie, K., Ding, X., Dang, L., Sun, J., Shi, F., Xu, H., Jiang, R., He, X., Liu, Z., Lei, Z. (2018) Highly Compressible Carbon Sponge Supercapacitor Electrode with Enhanced Performance by Growing Nickel-Cobalt Sulfide Nanosheets. *ACS Appl Mater Interfaces*, 10(12),10087-10095.
106. Yuan, C., Li, J., Hou, L., Zhang, X., Shen, L., Lou, X.W.D. (2012) Ultrathin Mesoporous NiCo₂O₄ Nanosheets Supported on Ni Foam as Advanced Electrodes for Supercapacitors. *Advanced Functional Materials*, 22(21),4592-4597.

AUTOBIOGRAPHY

Name Surname: Özlem BUDAK

T.C. Identity Number: 21239199860

Birth-date: 10.03.1990

Birth-place: Silivri- İSTANBUL

E-mail : ozlem.budak@marmara.edu.tr

EDUCATIONAL BACKGROUND

2008- 2012 Gazi University

Engineering Faculty Chemical Engineering Department

Records:

YDS : 88.75

ALES : 84.48

WORK EXPERIENCE

04.08.2014-18.12.2015 Kablotek Kablo San. ve Tic. Ltd. Şti

25.01.2016- 14.02.2018 Etimaden Kırka Bor İşletmeleri Müdürlüğü

15.02.2018- Marmara University Engineering Faculty Chemical Engineering Department- Research Assistant

PROJECT EXPERIENCE

FEN-C-YLP-250919-0275 Süperkapasitör Performansında Çeşitli Parametrelerin Analizi, Marmara University, Researcher

CONGRESS/CONFERENCE

Analyses on Electrochemical Properties of NiCo₂O₄ Supercapacitor Electrodes, The 3rd International Conference on Applications in Chemistry and Chemical Engineering (ICACChE) September 2019 in Skopje, North Macedonia.

Özlem BUDAK, Prof. Dr. Atıf KOCA