



Faculty of Sciences
Department of Chemistry and Forensic Sciences

**CATTLE BLOOD WASTE DERIVED CARBON@NICKEL COBALTITE
COMPOSITE FOR SUPERCAPACITOR APPLICATIONS**

by

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DECLARATION REGARDING THE WORK AND COPYRIGHT

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DEDICATION

I devote this research study to my wonderful beloved mother ‘Galenkgathe Matlho’ and grandmother for their undying support and for teaching me to work hard for what I want to achieve.

ABSTRACT

As fossil fuels become scarce, supercapacitors are a potential solution for storing energy from renewable sources, e.g. wind and sunlight for future use. The progression of supercapacitors necessitates the use of economical, plentiful, eco-friendly, and long-lasting electrode materials. Previous research has investigated the use of carbon obtained from different biomasses (basswood, biogas slurry, cow dung, rotten carrots, etc.) as electrode materials, as well as metal oxides (iron-based, cobalt-nickel-based, manganese-based, and vanadium-based electrode materials). This research work makes a significant contribution to the development and evaluation of activated carbon and new composite materials for supercapacitor electrodes as well as the preparation methods thereof. The conversion of cattle blood waste into activated carbon materials in this study provides an economical and feasible method to produce electrode materials for electric double layer (EDLC) and pseudo-supercapacitors. To generate activated carbon materials, cattle blood waste was dried, followed by carbonization under N_2 atmosphere and the resultant samples were chemically activated using KOH. The effect of physiochemical parameters of electrode materials on electrochemical performance was investigated. X-ray diffractometry showed that, samples lost their crystallinity, resulting in amorphous/turbostratic carbon materials with increase in activation ratio, time, and temperature. Raman spectroscopy showed that introducing KOH to carbonised materials induces structural defects. Using nitrogen sorption studies portray a decrease in pore volumes from 0.19 to $0.08\text{ cm}^3\text{ g}^{-1}$ and surface area from 340 to $140\text{ m}^2\text{ g}^{-1}$ as the activation KOH ratio increased from 1 to 3. Cyclic voltammetry (CV), cyclic charge-discharge (CCD), and electrochemical impedance spectroscopy (EIS) measurements were used to assess the capacitive properties of the electrode materials. Electrochemical measurements performed under three-electrode system revealed that the charge-discharge time and specific capacitances increased with decrease in carbonisation and activation temperature, time, and activation ratio. A sample carbonised at $800\text{ }^\circ\text{C}$ for 60 min and activated with KOH ratio 1:1 at $600\text{ }^\circ\text{C}$ for 30 min attained specific capacitance of 162.51 and 204 F g^{-1} at 5 mV s^{-1} scanning rate and current density of 0.5 A g^{-1} , respectively. The presence of micropores in the carbon framework showed a significant contribution to the specific capacitance of supercapacitor electrodes. When tested in a symmetric real device for supercapacitors, the above electrode exhibited ideal capacitive behaviour with an energy density of 20 Wh kg^{-1} and a power density of 4000 W kg^{-1} using 6 M KOH as electrolyte. All samples exhibited significantly low solution resistance, R_s , of 0.20 ohms , which improved electrolyte ion diffusion in the electrode's outer shell resulting in high power density. The electrode demonstrated displayed impressive cyclic

stability at 0.2 A g^{-1} after being cycled 5000 times with capacitance retention and coulombic efficiency of 91 percent and 100 percent, respectively. Furthermore, nickel-cobaltite (NiCo_2O_4) nanomaterial was incorporated into the optimum activated carbon, namely, ACBW11600_30, yielding an optimum composite with substantial specific capacitances of 431 F g^{-1} and 554 F g^{-1} at 5 mV s^{-1} and 0.5 A g^{-1} , respectively. NiCo_2O_4 is not only non-toxic and environmentally user-friendly, and it is also inexpensive to produce due to its abundant constituent metals. Finally, the use of blood waste provides a green synthetic method for activated carbon nanomaterials and has the potential to increase the economic value of slaughterhouse blood.

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LIST OF ABBREVIATION

AC	Activated Carbon
ACBW	Activated cattle blood waste
BET	Brunauer–Emmett–Teller
CBW	Cattle blood waste
CCD	Cyclic Charge Discharge
CNF	Carbon nanofiber
CNT	Carbon nanotube
CV	Cyclic Voltammetry
DFT	Density Functional Theory
EDL	Electric Double Layer
EDLCs	Electric Double Layer Capacitors
EIS	Electrochemical Impedance Spectroscopy
ESR	Equivalent Series Resistance
FAAS	Furnace atomic absorption spectroscopy
FTIR	Fourier transform infrared
HCNFs	Hollow carbon nanofiber
HEVs	Hybrid Electric Vehicles
NCs	Nanocubes
PENG	Piezoelectric nanogenerators
PVDF	Polyvinylidene difluoride
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
TMO	Transition metal oxides
XRD	X-ray diffraction analysis

Notations

C_{sp}	Specific capacitance ($F\ g^{-1}$)
R_{ct}	Charge transfer resistance (ohms)
t	Discharge time (s)
m	Mass of active material (g)
E	Energy ($W\ kg^{-1}$)
P	Power ($Wh\ kg^{-1}$)

Greek symbols

Δ	Delta
$^{\circ}$	Degree
$\int$	Integral

THESIS FRAMEWORK

The overall thesis framework is sectioned into five main chapters, summarized as follows:

- i. Chapter One outlines the introductory section, especially the background of electrochemical storage devices and electrode materials used for supercapacitors, motivation/purpose, problem statement, aim and specific objectives, research questions and significance.
- ii. Chapter Two presents a review of literature on energy storage devices, which are needed to solve issues of environmental pollution and fossil depletion by storing energy harnessed from solar and wind power. Supercapacitors are reviewed as a better choice than batteries and traditional capacitors because of high energy storage capacity and power density. Because of their high energy storage capacity and power density, supercapacitors are thought to be a better choice than batteries and traditional capacitors. Furthermore, the electrode materials suitable for supercapacitor high performance are explained.
- iii. Chapter Three is composed of the methodology and materials used to achieve the objectives of the work.
- iv. Chapter Four entails results and a discussion of the results of the work conducted in this study. The obtained results including characterizations and electrochemical performance testing are discussed from a scientific standpoint.
- v. Chapter Five summarizes the key conclusions, describes the scientific significance of the study, and suggests critical recommendations on future work.

1 INTRODUCTION

1.1 Background

Due to the continued growing global energy challenge, researchers have turned to renewable sources such as sunlight and wind [1]. To properly store the energy obtained from these resources, energy storage frameworks are required [2]. The most common types of energy storage devices are batteries and supercapacitors [3]. Mobile phones, personal computers, cameras, and electronic calculators are all powered by batteries. This allows people to work away from homes and offices. Batteries suffer from poor cyclic life stability and low charge-discharge rates despite having great energy densities. However, supercapacitors are emerging energy storage systems [4] because of their lengthy discharge cycles, outstanding power densities, fast charging/discharging rate, and overall safety [5]. Their high-power density makes them ideal for regenerative braking systems in automobiles, wind turbines, and hybrid electric vehicles. Pseudocapacitors, hybrid capacitors, and electric double-layer capacitors (EDLCs) are three types of supercapacitors that store energy in different ways [6]. Electrostatic ion interaction at the electrolyte-electrode interface stores energy in EDLCs, whereas electron charge transfer between electrode and electrolyte stores electrical energy faradaically or electrochemically in pseudocapacitors [7]. In hybrid capacitors, energy is stored electrostatically and electrochemically. Carbon-based materials are mainly used as negative electrodes in EDLCs because of their high electrical properties, high surface areas, and cost-effectiveness [8], [9]. Porous carbon obtained from biomass sources such as fibres of oil palm empty fruit bunches [10], bamboo [11], millet straw [12], basswood [13], lignocellulosic [14] and quinoa [15] has recently been used in supercapacitor applications. Thus, carbon-based electrodes have gotten enormous attention because of their sustainability credentials, availability, and affordability [16] but they suffer from low capacitances.

Every day, many cows are slaughtered in countries such as Botswana, and blood, an unavoidable by-product of beef production, is produced in large quantities, which may cause wastewater pollution problems if discarded directly into the environment. As a result, it is critical to converting abattoir waste feedstocks into value-added products. To some extent, blood waste and its by-products have been studied especially for use in agriculture and the feed industry [17] [18]. Slaughterhouse cow blood waste is inexpensive and rich in carbon, and thus a prospective carbon source for supercapacitor electrode materials. Carbon derived from cow

blood waste is known to possess large amounts of other elements such as oxygen, iron (Fe), potassium, and sodium [19]. Several articles have highlighted Fe sites as a possible active centre for electrochemical reactions [20]. Additionally, iron has a diverse variety of oxidation states, complex redox chemistry, and a wide range of potential windows which promotes high specific capacitance in supercapacitors [21] [22], [23]. Moreover, the preparation of iron-containing carbon electrodes often requires the use of two precursors: one for the carbon and the other for Iron. [24], [25]. However, in this study iron-doped carbon electrodes were obtained without the use of a Fe precursor. Carbonisation temperature, time, activation ratio, temperature, and time all influenced the electrode materials' surface area, morphology, pore size, porosity, and structural stability. The effect of pores, surface area, and electrochemical properties (phase angle, charge transfer resistance) on specific capacitance, cyclability, coulombic efficiency, capacity retention, power density, and energy density was investigated.

Oxides of iron [22], cobalt-nickel [26], [27], manganese [28]–[30], and vanadium are the most transition metal oxides previously studied as electrode materials for pseudocapacitors. These oxides however have low electrical conductivity but good redox behavior that favors pseudocapacitance. These oxides can, however, be combined with highly electrically conductive carbon materials that have wide surface areas, which provide electrical double-layer capacitance. This research study also focuses on activated carbon@NiCo₂O₄ composites as electrode materials for hybrid supercapacitors, where nickel cobaltite and activated carbon serves as pseudocapacitive and EDLC materials, respectively. NiCo₂O₄ was utilised in this study because of its high theoretical capacitance, simplicity of production, availability of raw materials, and non-toxic individual metal oxide precursors [31]. NiCo₂O₄ also has rich pseudocapacitive redox reactions originating both from cobalt and nickel that improve the performance of carbon. Additionally, NiCo₂O₄ stores energy both near and on the electrode surface, displaying promising pseudocapacitance behaviour [32]. To the best of our knowledge, no extensive research has been conducted on electrode materials for supercapacitors made from carbon derived from cattle blood waste. Utilisation of cattle blood to yield carbon-based active material for supercapacitors increases the economic potential of slaughterhouse blood while alleviating ecological concerns about groundwater pollution. Lastly, activated carbon derived from cattle blood waste has not been used in conjunction with NiCo₂O₄ as electrode materials for hybrid supercapacitors.

1.2 Statement of Problem

Hybrid and electric vehicles are becoming more mainstream, and by 2035, they are expected to account for the largest share of new automobiles [33]. Supercapacitors are used as auxiliary devices to store energy while decelerating and to offer the needed boost during rapid accelerations, resulting in increased vehicle efficiency [34]. However, a supercapacitor's performance is primarily influenced by the electrode materials employed. Whilst biomass-based electrode materials have been developed, they still have low capacitances. Transition metal oxides, on the other hand, have low electrical conductivity but high capacitance, which compensates for the shortcomings of carbon-based materials when composited. Thus, necessitating the development of materials that are inexpensive, abundant, and capable of resolving capacitance and energy density issues.

Because beef is Botswana's most important agri-food enterprise, 8,000 cattle are slaughtered daily, resulting in large amounts of blood produced, which may cause wastewater issues when discarded directly into the environment. This amount of cattle blood waste is sufficient for bulk porous carbon synthesis for low-cost electrochemical capacitors. Furthermore, converting cattle blood waste into carbon electrode materials aids in mitigating environmental concerns about groundwater pollution. Hence, this study explored porous activated carbon derived from cow blood composited with NiCo_2O_4 as supercapacitor electrodes that exhibit high specific capacitance, low charge transfer resistance, and improved energy density.

1.3 Objectives

1.3.1 General Objectives

To develop activated carbon derived from cattle blood waste and activated carbon@nickel cobaltite composite electrode materials for supercapacitors.

1.3.2 Specific Objectives

1. To synthesize and characterize cattle blood waste-derived activated carbon materials.
2. To investigate the effect of temperature on carbonisation process and chemical activation conditions on physicochemical parameters and electrochemical performance of the cattle blood waste-derived activated carbon electrode materials.

3. To synthesize and characterize the Activated carbon@NiCo₂O₄ composite electrode materials.
4. To assess the impact of the incorporation of metal oxide on activated carbon and its electrochemical performance.

1.4 Research Questions

1. What are the physical and chemical characteristics of the activated carbon material electrodes synthesized from cattle blood waste?
2. What effect do synthesis conditions and physicochemical properties have on the electrochemical performances of activated carbon composite electrodes sourced from cattle blood waste?
3. What are the physical and chemical characteristics of activated carbon@NiCo₂O₄ composite?
4. What is the influence of the incorporation of NiCo₂O₄ on the electrochemical performance of cattle blood waste-derived activated carbon?

1.5 Significance of the Research

This research explored the use of activated carbon@NiCo₂O₄ composites as a supercapacitor electrode material. Converting cattle blood waste into activated carbon offers an opportunity to reduce wastewater pollution and increase the economic value of slaughterhouse blood. The use of nickel-cobaltite serves as an alternative to toxic and expensive metal oxides such as ruthenium oxide. As a result, this environmentally friendly approach is needed to solve energy issues around the world. Botswana is Africa's greatest beef exporter, ranking 18th in the world, with eight thousand cattle slaughtered daily. It produces tonnes of beef, which is the country's key component of the agri-food economy. This amount is sufficient for the low-cost manufacturing of activated carbon materials for electrochemical devices such as supercapacitors. Furthermore, for a huge portion of the country's population, this will be a potential source of income.

1.6 Thesis overview

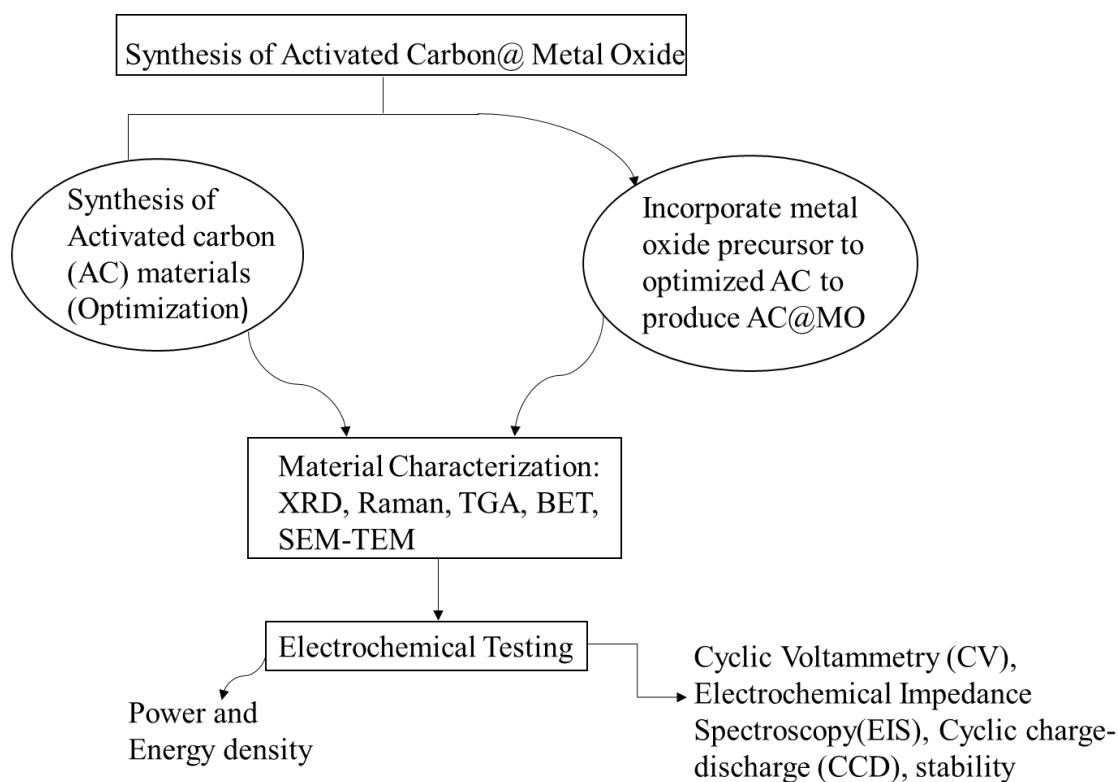


Figure 1: General experimental work summary of this research work.

2 LITERATURE REVIEW

2.1 Introduction on Electrochemical Energy Storage Technologies

Battery technology, fuel cells, supercapacitors, and other electrochemical energy storage systems are critical for the economic shift away from fossil fuels and towards renewable energy sources such as sunlight and wind [35]. Supercapacitors have extended cycle life and capacity to supply high power, and thus they are still a vital part of the energy storage industry. They can thus meet the demands for both high energy and low power density of both current and future technologies ranging from hybrid automobiles to portable devices. Supercapacitors have an extremely low energy density compared to fuel cells and commonly used lithium-ion cells. As a result, the issue of low energy density must be solved for supercapacitors to compete while still retaining their benefits of high power density, long cyclic stability, rapid charge and discharge capabilities, and wide working temperature range [36].

2.2 Applications of Energy Storage Devices

There are countless uses for supercapacitors, some of which are mentioned in the subsequent sections. Supercapacitors store and discharge energy quickly, making them extremely efficient.

2.2.1 Transportation

Used for regenerative braking purposes: Current electric vehicles can recycle kinetic energy into electrical power by using the motor as a generator while braking [34], [37]. Supercapacitors have long been used in regenerative systems for hybrid electric vehicles (HEVs) in racing sports [38]. The regenerated braking power is also used as an electric supercharger option for the conventional Mazda 6 and 3 [39].

Supercapacitors are used as an auxiliary source of power in today's fuel cell vehicles, including the Hyundai Tucson, Chevrolet Equinox, and Toyota FCHV [40]. Because fuel cells alone are frequently insufficient for accelerating either all-electric or hybrid vehicles, supercapacitors are used. Supercapacitors have proven to provide improved fuel economy and power-to-weight ratios than enlarging hydrogen fuel cells to increase acceleration.

There are several ways that supercapacitors can improve HEVs' fuel efficiency. Modern hybrid vehicles often completely switch down their engines when they stop, then restart them very efficiently utilising energy from supercapacitors [41]. Over 600,000 hybrid electric vehicles

employ supercapacitors in their stop-start systems. Supercapacitors can also serve as an alternative to lead acid batteries in traditional vehicle batteries.

2.2.2 Consumer Electronics, Military, and Aircraft

Coleman's portable cordless screwdrivers, powered by supercapacitors, are currently available for home use. This power tool charges in 90 seconds and is ready for use right away [42]. In both military and aerospace, supercapacitors are beneficial because they are long-lived and provide high power output. For military applications such as armed vehicles, helicopter black boxes, GPS-guided missiles, and other applications that require alternative power sources, supercapacitors are widely used [43]. In aircraft transportation, supercapacitors can be used as an auxiliary power source for aviation start-up systems, giving enormous bursts of current to the engines in a matter of seconds [44].

2.2.3 Energy harvesting

Energy harvesting innovation is based on the notion that systems can instantly capture and use energy from their surroundings, implying that energy is only ever temporarily stored [45]. Because of its quick charging, a supercapacitor is extensively used especially in combination with an energy harvester to store energy. Wearable piezoelectric nanogenerators (PENG), for example, have the potential to directly convert mechanical energy from human movement into electrical power [46]. The scavenged energy is stored in patterned electrochromic supercapacitors, which can be used in wearable electronics.

2.2.4 Medical devices

Implanted medical devices such as implantable neurostimulators, drug delivery systems, artificial cardiac pacemakers, and insulin pumps are powered by a supercapacitor and battery combination (supercapattery) [47]. During a cardiac emergency, cobalt phosphate-based piezoelectric devices have been used to produce electrical energy from the mechanical energy of heartbeats to power the pacemaker's circuit board and deliver electrical currents (self-rechargeable pacemakers) [48]. The device is expected to work successfully, consistently, and safely inside the human body for at least 15–20 years.

2.3 Energy and Power

Energy and power are typically used to describe the capabilities of any energy storage device [49]. Energy storage is critical for applications such as electric vehicles and portable electronics [50][51]. The energy density (Wh kg^{-1}) indicates how far one can go on a single charge, and the power density (W kg^{-1}) indicates how fast one can go [52]. The Ragone plot was devised

to compare the capacities for power and energy. An abstracted Ragone plot (Figure 2) reveals that capacitors can be thought of as high-power systems while storing insignificant amounts of energy [53]. In contrast, batteries store a reasonable amount of charge but release charge slowly [54], whereas supercapacitors provide a unique combination of high power and high energy properties, overcoming any barrier between batteries and capacitors [55],[56]. They have greater energy storage capacity than capacitors and reach a maximum power than battery systems.

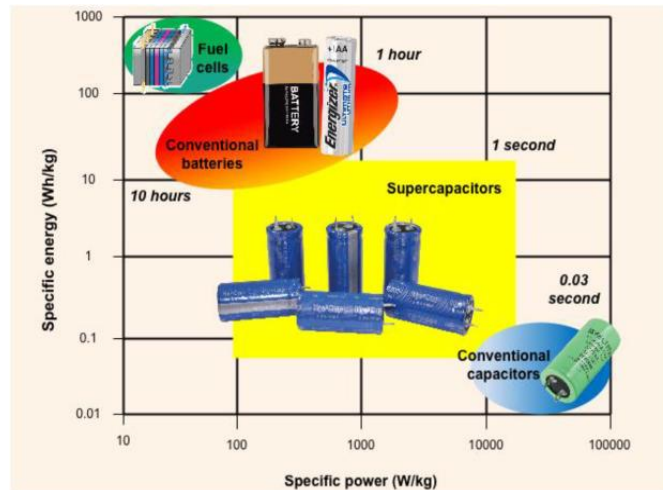


Figure 2: Ragone plot for energy storage devices [32]

2.4 Batteries versus Supercapacitors

Although batteries have great energy densities, they have poor cyclic stability, safety issues, and a slow rechargeable rate [58],[59]. Supercapacitors also referred to as ultracapacitors, provide outstanding specific power density, extended cyclic life, prompt charging/discharging, and higher energy efficiency of 90-95 percent than ordinary capacitors and batteries [60],[61]. Even though supercapacitors are potential high-energy storage technology, their specific energy is still low when compared to batteries [62]. Consequently, it is vital to develop high-performance anode materials that are small, dependable, energy-dense, charge quickly, and have long cycle and calendar lives.

2.5 Supercapacitors

An ordinary capacitor comprises two metallic plates/electrodes and an insulating material (dielectric) between them [63]. Capacitors gather opposite charges on two opposing conductive surfaces to store energy. Between the plates, an electric field arises, which can be utilized to swiftly store energy [64]. Because of a voltage difference between two plates holding charge $+q$ and q , a device capable of storing electrical energy according to the formula $G = \frac{1}{2} CV$ [65],

where G is the Gibbs free energy and C is capacitance (expressed in Farads, F). Supercapacitors have several times the capacitance of regular capacitors and can deliver higher power density (10-100 times that of batteries), more than 5 Wh kg^{-1} specific energy density, and thousands of charge cycles [66]. Supercapacitors are devices that store energy. With the help of a permeable layer, energy in supercapacitors can be stored between two high-surface-area electrodes without posing a risk of short circuits [66]. An electrolyte solution is used to transmit the charge between the two active electrodes [63]. One electrode is positive, and the other is negative. When the electrolyte is charged, the ions migrate to their respective electrode surfaces, and form an electric double layer at the electrolyte-electrode boundary, as depicted in Figure 3 [67], [68].

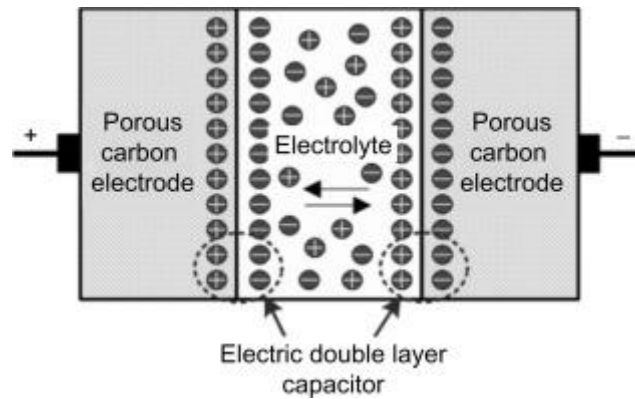


Figure 3: A depiction of a charged electrochemical capacitor and the formation of an electric double layer at the electrode-electrolyte interface [68]

2.5.1 Capacitive Energy Storage Principle in Supercapacitors

Supercapacitors employ two basic energy storage principles: double-layer electrics and pseudo-capacitance [69].

By polarizing an electrolytic solution, energy is stored in EDLCs through electrostatic interactions with no chemical reactions taking place [70]. As a result of this reversible phenomenon, supercapacitors can be charged and discharged at quick speed over an extended period [71]. In most cases, high porosity and surface area carbon-based electrode materials are utilised in EDLC owing to their exceptionally high electrical conductivity.

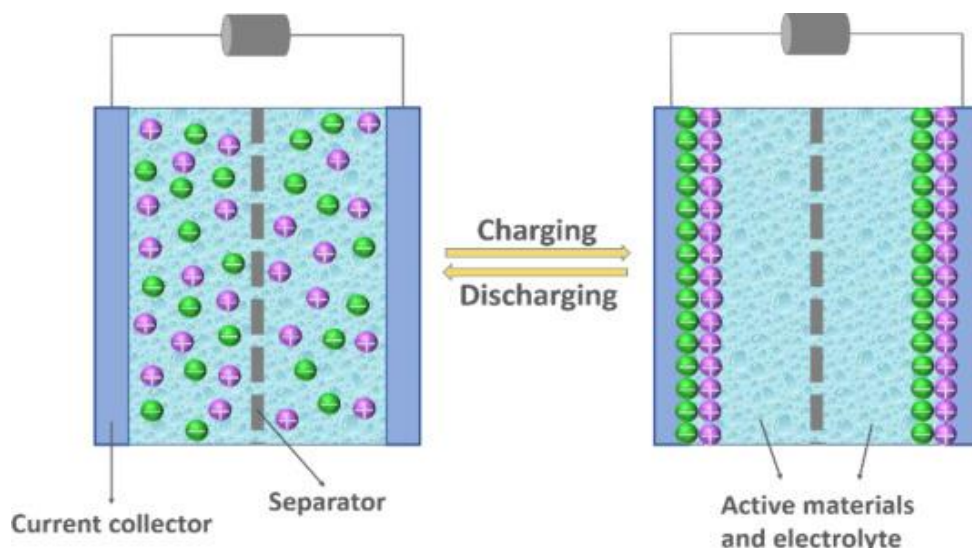


Figure 4: charge-discharge storage EDLC mechanism [72]

As a means of storing charge, when a potential is applied to pseudocapacitors, reversible redox reactions (faradaic reactions) take place, which include fast electrolyte deposition on electrode surfaces [73]. The charge is carried through a Helmholtz double layer, causing a reversible redox current to flow through the supercapacitor cell [74]. The mechanism of charge and discharge of a pseudocapacitor is more like that of batteries. In contrast to EDLCs, these processes in supercapacitors increase the energy density and specific capacitance [75]. On the contrary, pseudocapacitors have poor cycling life stability and low output power [73]. Conducting polymers and metal oxides are pseudocapacitive materials that provide redox reactions.

2.5.2 Supercapacitor Electrode Materials

The physicochemical characteristics of electrode materials, which include their morphology, surface area, porosity, pore size, and structural stability, have a great impact on the electrochemical performance of EDLCs and pseudocapacitors, especially their cyclability, specific capacitance, and energy density. Most supercapacitor electrodes available at present are made from activated carbon derived from biomass, carbon nanotubes [76], graphene, carbon foam, and carbon aerogel. High specific surface area, exceptional conductivity, low electrical resistance, and structural stability all play a role in their selection. Nevertheless, their use in supercapacitors is limited due to their small capacitances and poor cycle stability. However, by combining hydroxides and transition metal oxides, functionalized carbon, conductive polymers, and their composites, carbon-based materials' specific capacitance can be improved. Table 1 gives a summary of electrode materials for EDLC and pseudocapacitors.

Table 1: Common EDLC and pseudocapacitor electrode materials

EDLCs	Pseudocapacitors
Nitrogen-enriched graphene-like carbon nanosheets from bio-oil [77]	NiCo ₂ O ₄ /MnO ₂ nanorods[78]
Millet straw activated carbon and anthracite coal activated carbon[12]	Nitrogen doped RGO/CNT/MnO ₂ [79]
Carbon foam from resorcinol–formaldehyde[80]	Carbon fiber/NiFe ₂ O ₄ [81]
Activated carbon derived from rotten carrot[82]	Nickel oxide/carbon nanotube composite [83]
Biobased carbon aerogels decorated with Graphene dots [84]	FeCo ₂ O ₄ Microspheres and Nanosheets [85]

2.5.2.1 Biomass-derived porous Activated Carbon

Many applications have employed activated carbon (AC) with large surface areas, including water treatment [86], poison treatment, pharmaceuticals, food and beverage, and electrical storage. ACs were historically made primarily from coal and petroleum, along with their functionalized derivatives (carbon nanotubes, carbon aerogel, graphene, carbon foam). However, due to pollution and the limited supply of non-renewable energy sources, scientists are continuing to investigate organic wastes as feasible raw materials to produce AC. Biomass-derived porous carbon maintains a competitive edge in supercapacitors applications because of its eco-friendliness, inexpensiveness, high specific surface area, good electric electrical characteristics, high cycling stabilities, and environmental sustainability. These distinct qualities have grabbed the attention of numerous researchers.

For example, chemical (KOH) activation of biogas slurry at 700 °C for 120 min at a 3:1 KOH/carbon to mass ratio produced mesoporous carbon materials with 4.4 nm pore diameter. Consequently, mesopore, micropore, and specific surface areas (S_{BET}) for the material were determined by Enock *et al.*, to be 165, 350, and 515 m² g⁻¹, respectively [87]. Using three electrodes and 6 M KOH as electrolyte, 289 F g⁻¹ specific capacitance was achieved at 5 mV s⁻¹.

Recently, sisal-derived carbon fibers KOH-activated at 750 °C were shown to exhibit high S_{BET} and pore volume of 2289 m² g⁻¹ and 1.23 cm³ g⁻¹, respectively. This S_{BET} is one of the

parameters that contributed significantly to the observed promising specific capacitance of 415 F g⁻¹ at 0.5 A g⁻¹, and 93% capacitance retention after 10,000 cycles at 10 A g⁻¹ conducted in 6 M KOH [88]. Rajasekaran and Raghavan synthesized KOH-activated carbon derived from Eucalyptus globulus seed, which showed 2388.38 m² g⁻¹ large S_{BET} and 150 F g⁻¹ specific capacitance. Despite the large specific surface area, the low specific capacitance was recorded. This means that specific surface areas, do not exclusively contribute to exceptional capacitances.

Scientists are interested in biomass-based carbon materials for a number of reasons, including their availability, affordability, large specific areas, and excellent stability. Still, they have low capacitances, capacities, and energy densities. Investigating the link between surface chemistry and specific capacitance will improve the performance of these porous materials [89]. As part of surface chemistry, particle size distribution, pores volumes, and interconnectivity are considered [90].

The doping of electrode materials with heteroatoms can increase surface wettability [28], lower charge transfer resistance, and add pseudo-capacitance to the dominant EDL capacitance, among other benefits. In EDLC electrodes, both naturally occurring and synthetic heteroatom-doped carbon have been used for performance enhancement especially in addressing the low energy density problem. Several researchers have made use of synthetic heteroatom doping of carbon materials [91]. Unfortunately, this method is labor-intensive and costly, and it necessitates the use of hazardous precursors like ammonia, pyrrole, and hydrazine. As a result, self-doped heteroatom carbon material remains the most popular electrode material for EDLC because of its inexpensiveness and environment benign.

A one-step procedure was used by Zhao *et al.*, to make nitrogen, phosphorus, and sulfur self-doped hierarchically porous carbon (N-P-HPS) from peanut meal. The N-P-HPS had a specific surface area of 2090 m² g⁻¹ and contained 11.2% nitrogen, 0.82% phosphorus, and 0.6% sulphur [92]. This carbon also demonstrated a very high specific capacitance of 525 F g⁻¹ and a maximum energy density of 24.9 Wh kg⁻¹ at 400 W kg⁻¹ power density. Chen *et al.*, exploited Elm blossom-sourced biomass to hydrothermally prepare nitrogen and sulphur containing activated carbon before chemical activation with KOH. Owing to a high S_{BET} of 2048.6 m² g⁻¹, a reasonable pore volume of 0.83 cm³ g⁻¹, and high N (2.2%) and S (6.06%) concentrations resulted in a respectable specific capacitance of 275 F g⁻¹ at 1 A g⁻¹ [93]. After 5000 cycles at

4 A g⁻¹, the maximum energy density and power density were 16.8 Wh kg⁻¹ and 600 W kg⁻¹, respectively, with capacitance retention of 87.2%.

2.5.2.2 Transition Metal Oxides

Good supercapacitor transition metal oxide (TMO) materials have low electrical resistance, multiple oxidation numbers, and pseudocapacitive behaviour with high specific capacitances. TMOs that has previously been studied as electrode materials for supercapacitors are ruthenium (IV) oxide (RuO₂), vanadium (V) peroxide (V₂O₅), cobalt (III) oxide (Co₂O₃), nickel (II) oxide (NiO), manganese (IV) dioxide (MnO₂), and iron (III) oxide (Fe₂O₃) as electrode materials. Ruthenium is a prominent material exhibiting high specific capacitance, wide operation voltage window, low electrical resistance, long cycle life, and multiple reversible redox states [94],[95],[96]. However, due to RuO₂'s relatively high cost, restricted rate capability, and toxic properties, cost-effective TMOs such (as Co₂O₃, NiO, MnO₂, and Fe₂O₃) have emerged [97].

Manganese is the second-most abundant transition metal on Earth, and due to its physicochemical similarity to that of iron, manganese is an essential micronutrient for most living organisms. In comparison to iron (53 000 ppm), the Earth's crust contains approximately 1000 ppm Mn; the atomic weight (54.94) is comparable to iron (55.85) [98]. Manganese oxides (MnO_x) have sparked a lot of interest due to their inherent differences in redox characteristics, morphology, crystalline structure, and surface nanoarchitecture. Furthermore, MnO_x has been identified as a potential electrode material for supercapacitors due to its availability, inexpensiveness, non-toxicity, and maximum theoretical specific capacitance of 1370 F g⁻¹ [99], [100].

MnO₂-coated carbon nanotube-embedded carbon nanofiber core-shell cables have been manufactured, delivering 483.5 F g⁻¹ specific capacitance in 1 M Na₂SO₄ solution at 0.5 A g⁻¹. The asymmetric supercapacitor reached a maximum power density of 1000 W kg⁻¹, an energy density of 209.4 Wh kg⁻¹, and a specific capacitance of 94.25 F g⁻¹ at 0.5 A g⁻¹ and 4.0 V [101].

Theoretically high specific capacitance (3560 F g⁻¹), exceptional redox characteristics, and inexpensive price make cobalt oxide a promising electrode material. Their low conductivity and short cycle life, on contrary, limit their application [102]. Its structural integrity is also compromised by its tendency to expand and contract during a charge-discharge cycle. To avoid these issues, it is employed in conjunction with conductive materials such as porous carbon materials [103]. Carbon materials are structurally stable, and have high electrical conductivity and large surface areas, all of which contribute to increased capacitance and durability [104].

In this regard, $\text{Co}_3\text{O}_4/\text{C}$ composites have been synthesized using the wet chemistry route. The composite $\text{Co}_3\text{O}_4/\text{C}$ evaluated in 1 M KOH delivered 567 F g^{-1} specific capacitance at 3 mV s^{-1} and maximum energy density of 63 Wh kg^{-1} . Furthermore, after 6000 cycles, a capacitive retention of 82% was recorded [105].

Controlling cobalt-based materials' size, surface, and texture morphologies, which impacts electrochemical performance, is a definite benefit [106][107]. The active electrode materials with nanoscale dimensions, such as small particle size and a high surface/volume ratio, are responsible for lowering ion and mass diffusion and providing more active reaction centres during the charging-discharging process.

Using a hydrothermal process, Jang created porous Co_2O_3 nanocubes (NCs) that were typically between 50 and 60 nm in size. With a 6 M KOH electrolyte present, the manufactured porous Co_2O_3 NCs provided an outstanding specific capacitance of 430.6 F g^{-1} at 10 mV s^{-1} and retained 85% of its initial capacitance after 1000 cycles [107].

Nickel oxide has since been reported as favourable electrode material for pseudocapacitors because of its inexpensive cost, high theoretical specific capacitance of 2573 F g^{-1} , and impressive reversible redox reactions [108]. The capacitive properties of NiO, predominantly depend on its morphology and structure [109]. Several techniques have been explored to modify the structure of NiO materials to improve their electrical properties.

Lai *et al.*, for example, created a multi-layered NiO/carbon nanotube composite with a specific capacitance of 713.9 F g^{-1} at 2 mV s^{-1} [83]. The inclusion of conductive carbon nanotubes network, which improved the nickel oxides' weak electrical conductivity and helped the transfer of electrons during charge/discharge operations, resulted in high specific capacitance. The supercapacitor displayed good stability with an 88.2% capacitance retention after 3000 cycles, as well as energy and power densities of 23.9 Wh kg^{-1} and 698.6 W kg^{-1} , respectively.

With its exceptional theoretical capacity, cost-effectiveness, enormous amount, and lesser ecological toxicity, iron oxide has served as a pseudocapacitor electrode material [110], [111]. Fe_3O_4 (magnetite), is thought to be an attractive pseudocapacitance material due to additional benefits such as a huge voltage window (0.25 to 1.2 V) and wide availability [112],[113].

Yu *et al.*, developed hybrids of iron oxide and hollow carbon nanofibers (HCNFs) for pseudocapacitor electrodes using a 3-steps procedure: concentric electrospinning, pre-

oxidization in a tube furnace, and carbonization [111]. Iron (III) acetylacetonate was used as a metal oxide precursor. The constructed HCNFs afforded a specific capacitance of 121 F g⁻¹ at 0.5 A g⁻¹ and 90% retention capacitance after 1000 cycles in 1 M sodium sulfite.

Despite researchers' attempts to synthesize iron oxides with activated carbon to produce composites with good properties, most iron oxide synthetic processes are complicated such as microemulsion, laser pyrolysis, and thermal decomposition method [114]. Additionally, external doping involves several phases, including pre-carbonization, activation, and doping, all of which are difficult, time-consuming operations. These synthetic approaches limit the commercial use of iron oxide/activated carbon composites while minimizing their mass production. Self-doping, on the other hand, produces heteroatom-doped carbon materials through direct carbonization of biomass sources. Therefore, this forms the basis of our study, where Fe self-incorporated activated carbon sourced from cattle blood waste was investigated for supercapacitor applications.

2.5.2.3 Ternary Metals Oxides

Ternary metal oxides have been studied among transition metal oxides due to their availability, high specific capacitance, and various oxidation states that allow for multiple redox processes. They are said to outperform single-component metal oxides in terms of supercapacitive performance. Ternary metal oxides (A_xB_yO_z) are divided into three categories: AB₂O₄, ABO₄, and A₃B₂O₈, where A and B identify metal elements with low and high oxidation states, respectively [102]. The metal elements A and B are important in the electrochemical energy storage process. Spinel structured oxides, with a typical formula of AB₂O₄, are gaining traction as viable electrode materials because of the contributions of both metals to charge storage.

NiCo₂O₄ has received the most attention because of its high electrical conductivity, less expensiveness, improved electrochemical activity, higher redox activity, and larger theoretical capacitance than the separate Co₃O₄ and NiO [115][116]. Microwave-aided synthesis[117], coprecipitation [118], electrodeposition [119], [120], hydrothermal [121], sol-gel [122] and electrospinning [123] methods have been reported for producing NiCo₂O₄. Among these technologies, the hydrothermal approach has received the most attention due to its availability, simplicity, and capacity to influence particle size and morphology [124].

Boopathi Raja *et al.*, [125] synthesized NiCo₂O₄ with various morphologies i.e nanosheets and nanoflakes via the hydrothermal treatment method. The NiCo₂O₄ nanoflakes exhibited an outstanding specific capacitance (1366 F g⁻¹ at 2 A g⁻¹) and capacitance retention (86.7%) after

5000 cycles in a three-electrode system. The asymmetric NiCo_2O_4 supercapacitor device achieved an ultrahigh energy density of 42.1 Wh kg^{-1} at a power density of 1193 W kg^{-1} .

Zhang *et al.*, created hierarchy mesoporous NiCo_2O_4 nanoneedle arrays on carbon cloth, using a hydrothermal treatment method and a post-annealing treatment [126]. A three-electrode configuration and a 2 M KOH electrolyte were used to evaluate the electrochemical performance of the arrays. A study revealed that at a current density of 2 A g^{-1} , the arrays exhibited a specific capacitance of 660 F g^{-1} . In addition, the composite maintained 91.8% of its capacitance after 3,000 cycles.

2.5.2.4 Carbon-Metal Oxide-based Hybrid Supercapacitors Materials

Several different composite electrode materials have been manufactured for hybrid supercapacitors, that may provide high specific capacitances, rate capability, extended cyclic stability, energy, and power density [127]. The composite material blends activated carbon, an electric double-layer capacitive material, with ternary and transition metal oxide(s), serving as pseudocapacitive electrode materials.

Rajasekaran *et al.*, produced MnO_2 -doped holey carbon materials and conducted the electrochemical test in the three-electrode configuration using 6 M KOH as electrolyte. After 10,000 cycles, the as-obtained electrode materials demonstrated outstanding capacitance retention of 91.67% at 10 A g^{-1} and 460 F g^{-1} specific capacitance at 0.2 A g^{-1} [128].

Oh *et al.*, utilized a reduction process to make oxidized AC/ Fe_3O_4 composites for hybrid supercapacitor electrodes. An increase in Fe_3O_4 content to (AC: Fe_3O_4) 1:5 was observed to have caused an increase in specific capacitance from 99.4 to 202.6 F g^{-1} for raw AC and AC/ Fe_3O_4 composites, respectively, at 10 mV s^{-1} . The average pore size of 1.64 nm for AC/ Fe_3O_4 was reported which is suitable for EDLC application [129]. Combining Fe_3O_4 and AC efficiently synergized the pseudo-capacitance and electrical double-layer capacitance qualities.

However, transition metal oxides have some disadvantages, such as low chemical stability and poor electrical conductivity [71]. Thus, it is essential to construct ternary or composite with other materials in the desired ratio in to increase the electrochemical effectiveness and long-term durability of the individual transition metal oxide. Many researchers, however, combine ternary metal oxides such as NiCo_2O_4 with carbon to improve their electrical conductivity and rate capability.

Kibona *et al.*, used chemical synthesis to create composites of NiCo₂O₄/mesoporous carbon-derived biogas slurry. For the sample annealed at 350 °C, the composite had a high specific capacitance of 835 F g⁻¹ at a 5 mV s⁻¹ scan rate. After 50,000 cycles, the electrodes had cyclic stabilities above 90%, because of additional electroactive sites are available for redox processes, and the porous structure of NiCo₂O₄ can overcome volume variations, improving capacity retention [32]. This reveals that the produced NiCo₂O₄/mesoporous carbon composites are best suited for supercapacitors.

2.5.3 Cattle Blood Waste: Potential Candidate for High-Performance Supercapacitors

Blood is an unavoidable offshoot of meat production, but due to the high volumes produced by slaughterhouses, it may cause wastewater problems if disposed of directly into the environment. As a result, there has been gaining popularity in transforming biowaste resources into high-value products. Some research has been conducted on blood waste and its by-products. Whole blood is utilized as a mild protein source in traditional foods like dark pudding and pet food, while plasma proteins are employed as emulsifiers [17],[130]. Components such as thrombin and plasma have been extracted from animal blood for medical purposes. Animal blood waste has been used in fertilizer production as well [131]. Lastly, animal blood has been used to some extent as a carbon material in various applications, such as polymer electrolyte fuel cells [132], hydrogen peroxide sensors, and Pro-drug activators [133]. In addition, iron self-doped carbon derived from pig blood waste has been reported to be useful as an electrocatalyst for Zinc-air batteries [134] and anion exchange membrane fuel cells [135] and nitrogen self-doped carbon catalyst for oxygen reduction [136].

There have been no reports on the utilization of carbon produced from cattle blood waste in supercapacitor applications, highlighting yet another benefit of using blood waste as a carbon source for electrode materials. A key component of animal blood such haemoglobin is known to comprise of four polypeptide chains (the group -CO-NH-), with each chain attached to a heme moiety made of porphyrin connected to iron in the ferrous state [137]. Haemoglobin which is nitrogen, iron, and carbon-containing makes the blood an extraordinary potential iron-carbon source for electrode materials.

CHAPTER THREE

3 EXPERIMENTAL APPROACH

3.1 Reagents and Materials

Iron standards and cobalt (III) chloride hexahydrate were purchased from Sigma Aldrich. Urea, sodium hydroxide, and methanol were obtained from Rochelle chemicals. Commercial activated charcoal (AC115), dimethylformamide, acetone, nickel chloride hexahydrate, hydrochloric acid, potassium hydroxide, and nitric acid were obtained from Alpha chem. MTI Corporation provided nickel foam, Kuray conductive carbon (Model YP-50F), and polyvinylidene difluoride (PVDF). The chemicals mentioned above were utilised without further pre-treatment.

3.2 Preparation of Activated Carbon (AC) Materials

Cattle blood waste (CBW) was collected from the Jago abattoir in Palapye, Botswana, using an open drain system. CBW was oven-dried at 100 °C for two days before being crushed into granules. The crushed CBW was carbonized in a horizontal tube furnace (MTI OTF-1200X-60 model) at 400-900 °C for 60 min (at a heating rate of 10 °C/min) in a nitrogen atmosphere (flowrate: 20.00 cm³/min). The mechanically powdered pyrolyzed materials were named CCBW_x_y, where x and y denote carbonization temperature and time, respectively. The powdered sample was then chemically activated with KOH at ratios (wt/wt) 1, 2, and 3, and at different activation temperatures and times in the tube furnace. The activated carbon was naturally cooled down to room temperature under the flow of nitrogen gas. Before drying overnight at 100 °C, the sample was immersed in a 1 M HCl solution for 6 h to neutralize the remaining KOH and remove ash. ACBW_{yx}_z designation was given to the activated samples, where y, x, and z represent the activation ratio, temperature, and time, respectively.

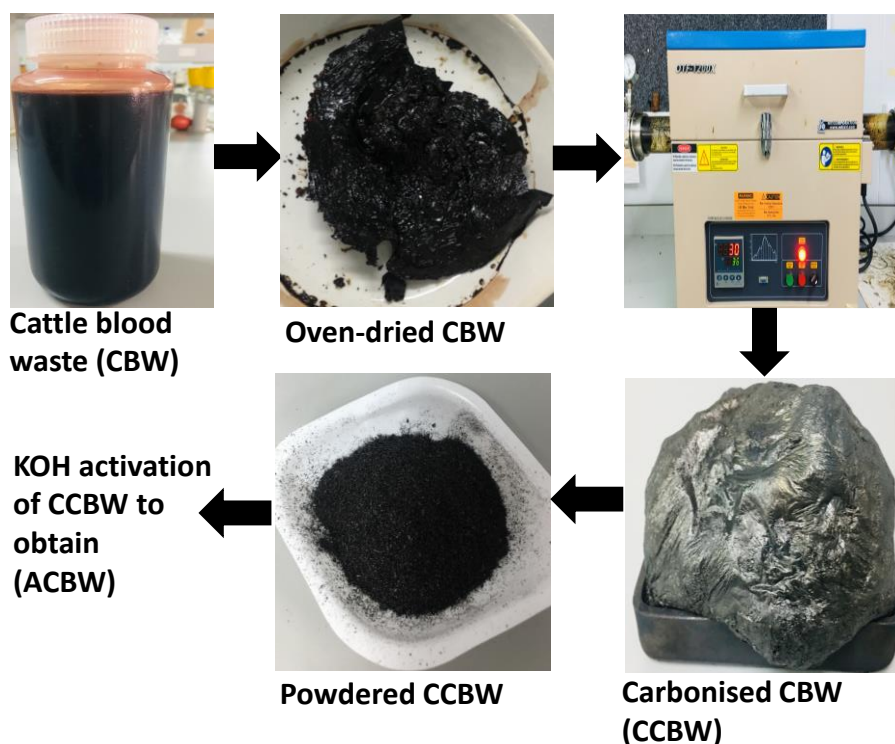


Figure 5: Activated carbon materials preparation process.

3.3 Synthesis of Activated carbon@Nickel cobaltite Composite Materials

Nickel chloride, cobalt chloride, and urea (1:2:15) were suspended in a combination of 40 mL distilled water and 40 mL methanol, then ACBW11600_30 (AC) was added and sonicated for 1 h. The mixture was transferred to a 100 mL hydrothermal vessel and closed tightly. The hydrothermal autoclave was heated at 140 °C constantly for 6 h, then allowed to cool naturally to ambient temperature. The precipitate was collected by suction filtration using a vacuum pump and oven-dried overnight at 100 °C. The resultant sample was given the name AC_x@NiCo₂O₄, where x represents the mass of carbon loading.

3.4 Characterization Techniques

3.4.1 X-ray Diffraction measurements

The crystal structure of the produced materials was studied using a Bruker D8 Advance powder diffractometer equipped with a Cu tube X-ray source and a Lynx Eye XE energy-dispersive strip detector. The radiation used was a Cu-K with a wavelength of 1.54056 Å that was applied in 0.02° increments for 0.500 seconds between 10 and 80°. The diffractometer operated at 40 mA and 40 kV.

3.4.2 Raman Spectroscopy

Raman spectroscopy was also used to determine the vibrational response of the samples. The Raman spectra were collected using a LabRAM HR800 Raman spectrophotometer and samples were excited using a 532 nm laser.

3.4.3 Nitrogen BET adsorption-desorption analysis

Nitrogen sorption is a technique that uses surface nitrogen adsorption to assess a material's BET-specific surface area, pore diameter, pore volume, and pore size distribution. The formation of a monolayer during the nitrogen adsorption process allows the specific surface area to be determined using the Brunauer – Emmett – Teller (BET) theory. When nitrogen partial pressure is increased by exposing the sample, capillary condensation occurs in the pores of the material, resulting in a significant increase in the quantity of nitrogen adsorbed. The pore volume/size and pore size distribution are measured in this region of the nitrogen sorption isotherm.

Nitrogen adsorption-desorption isotherms were obtained using Nova Touch LX2 surface area/pore size analyser equipped with Quantachrome TouchWin software at a temperature of liquid N₂ (77.35 K). The BET surface area of the synthesized materials was determined using the multipoint BET method, and the pore size distribution using the density functional theory (DFT). Other methods for obtaining a specific surface area from gas adsorption are based on the application of the standard isotherm concept, such as t- and α -plot methods, which allow one to obtain the external surface area. The micropore surface area can be calculated by subtracting the external surface area from the BET (total specific) surface area. The non-local density functional theory (NLDFT) method can calculate the specific cumulative surface area (i.e., specific surface area as a function of pore size) across the entire range of micro- and mesopores by differentiating between micro- and external surface area [138].

3.4.4 Scanning and Transmission electron microscopy

The morphology of the porous activated carbon materials was examined using Carl Zeiss FEGSEM Gemini 500 Field Gun-Scanning Electron Microscope (FEG-SEM) operating at an accelerating voltage of 5 kV and JEOL JEM-2100F electron transmission electron microscopy (HR-TEM) operating at 200 kV accelerating voltage.

3.4.5 Thermogravimetric analysis (TGA)

The thermal decomposition tendency of the as-synthesized materials was evaluated using a TGA/DSC3+ Mettler Toledo, thermogravimetric analyser. The thermal decomposition study

was conducted at temperatures ranging from room temperature to 1000 °C with a fixed ramp rate of 10 °C per min and a flow rate of 20 mL per min nitrogen.

3.5 Electrochemical characterization

Electrochemical tests were performed with a three-electrode system, with Hg/HgO, activated carbon@metal oxide composites (AC@MO), and platinum wire used as the reference electrode, working electrode, and counter electrode, respectively. To make the working electrode, the active materials, conducting carbon, and the binder (polyvinylidene fluoride, PVDF) were mixed in the following percentages to make the working electrode: 80:10:10. After that, the electrode materials were applied to nickel foam (1 cm²) at a mass loading of about 5 mg.

The electrochemical tests included cyclic charge-discharge (CCD), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and stability tests, which were conducted using a 6 M KOH electrolyte and Gamry Potentiostat/Galvanostat Reference 3000 instrument. Activated carbon and AC@NiCo₂O₄ materials were run between voltage windows of 0 to -1V and 0.15 to 0.55V, respectively.

EQ-HSTC split coin cells with Ni foam serving as the current collector and Whatman glass microfibre filters as separating material were used to build a symmetrical two-electrode cell. Before using the Whatman filter as separating material, the filter was soaked in 6 M KOH overnight. The two working electrodes were created by combining synthesized carbon material, PVDF, and conductive carbon at a percentage ratio of 80:10:10 in a mixture of acetone and DMF (1:2 volume ratio) to create a viscous slurry that was smeared on nickel foam pieces with an area of 3.14 cm². To evaporate the solvent, the electrodes were oven-dried overnight at 50 °C. The active material's total mass on the surface of the individual electrode was obtained by subtracting the mass of nickel foam before and after coating. The combined masses (both electrodes) of active materials ranged from 11.7 to 15.4 mg.

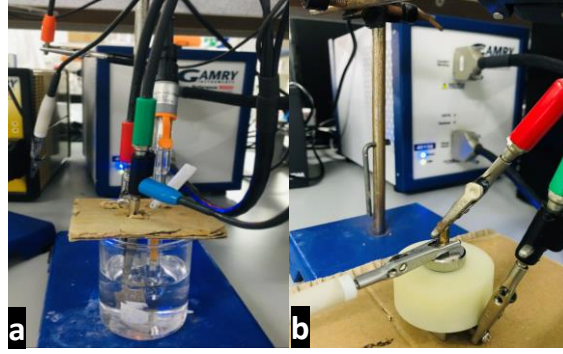


Figure 6: Cell construction for three-electrode and b) two-electrode setup

3.5.1 Cyclic Voltammetry

Cyclic voltammetry (CV) is one electrochemical technique that involves adjusting the applied voltage at a working electrode in both forward and backward directions (at a certain scan rate) while monitoring the current [139]. In practice, CV studies can be used to determine the working voltage or reversibility of charge-discharge operations and the specific capacitance of electrode materials [140]. The specific capacitance (C_s) was computed using equation 1 by integrating the area of CV curves at various scan rates ranging from 5 to 200 mV s^{-1} .

$$C_s = \frac{\int IdV}{2m \cdot \Delta V \cdot S} \quad (1)$$

Where $\int IdV$ is the quantified charge deduced by integrating the area of CV curves, m is the active material's mass (g), S is the scanning rate (V s^{-1}), I is the measured current (A) and ΔV is the working voltage window [112][141].

3.5.2 Cyclic Charge- Discharge (CCD)

CCD is a popular method for evaluating the performance and cyclic stability of EDLCs. Cycling involves repeated loops of charge/discharge at a steady current until a predetermined potential is attained. Using equation 2, the specific capacitance for the three-electrode system (F g^{-1}) was calculated from the CCD curve.[72].

$$C_{sp} = \frac{I \cdot \Delta t}{m \cdot \Delta V} \quad (2)$$

I denote the discharge current, Δt discharge period, m mass of active material, and ΔV the voltage window difference.

The specific capacitances for the two-electrode system were determined by using equation 3 from cyclic charge-discharge data:

$$C_{sp} = \frac{4I \cdot \Delta t}{m \cdot \Delta V} \quad (3)$$

where I denotes the discharge current (A), Δt is the discharge time (s), m is the total mass (g) of the active material and ΔV is the potential window (V).

3.5.3 Electrochemical Impedance Spectroscopy (EIS)

EIS is an electrochemical method used to investigate the electron-transfer characteristics and chemical transformations of surfaces [143]. It also gives mechanistic and kinetic data on batteries and supercapacitors. The electrical resistance of the electrode/solution interface is measured using an EIS at an amplitude of 10 mV and a frequency range of 0.01 Hz to 100 kHz. By carrying out the EIS, it is possible to determine the polarization resistance of the double layer (low-frequency zone), the solution resistance of the double layer (high-frequency region), and the capacitance of the double layer [144].

3.5.4 Stability Test, Power, and Energy Density

To determine the electrode materials' cycle life, cyclic stability tests were performed. The energy storage capabilities of the active materials were evaluated using symmetrical two-electrode systems. The following equations were used to calculate the energy density E (Wh kg^{-1}) and power density P (W kg^{-1}) [20] [27] of the electrode material for supercapacitors.

$$E = \frac{1}{2} C_{sp} (\Delta V)^2 \frac{1}{3.6} \quad (4)$$

$$P = \frac{3600 \times E}{\Delta t} \quad (5)$$

The capacitance of the two-electrode supercapacitor is given by C_{sp} (F g^{-1}), the voltage range for the charge and discharge process by ΔV , the discharging time by Δt (s), and energy density by E .

4 RESULTS AND DISCUSSION

4.1 Characterisation

XRD, Raman, FTIR, BET, and TGA techniques were used to investigate the physicochemical parameters of the generated porous carbon. This chapter presents and examines various electrode material characterizations and electrochemical measurements. It discusses how the electrochemical performance of activated carbon materials is affected by synthetic parameters. To assess the electrode materials' practical usefulness, this section examined several factors, including cycle stability, specific capacitance, porosity, power delivery, and capacity retention.

4.1.1 X-ray Diffraction measurements

4.1.1.1 Activated Carbon Materials

This section will discuss the XRD patterns of carbonized cattle blood waste (CCBW) and activated cattle blood waste (ACBW) samples, as shown in Figure 7 (a)-(d). The CCBW samples exhibited a broad characteristic peak at 25° due to graphitic carbon and crystalline peak at 45° , corresponding to the (002) and (100) lattice planes, respectively. Additional sharp diffraction peaks observed at 31.73 , 34.07 , 38.05 , 56.52 , and 66.13° corresponding to the reflection planes of (220), (311), (222), (511), (440) respectively were confirmed to be of Fe_3O_4 phase with a face-centered cubic structure. The intensity of the characteristic peak (311) was small for all samples due to the preferred orientation, which leads to the absence or weakening of certain peaks [145]. Impurity peak at 27.58° decreased as carbonisation temperature and time were increased. Figure 7b demonstrates that the minor peaks over 45° identified as iron or other existing contaminants disappeared when the activation KOH ratio increased from 0 to 3. This implies, that either KOH or HCl had etched away the iron and other impurities, resulting in the amorphous state of the samples. The degree of graphitization, on the other hand, improved as the KOH activation ratio increased. Figure ©, and d shows ACBW samples activated at different temperatures and time, respectively. The peak indexed (100) broadens with increasing activation temperature and time, owing to crystallinity loss (as shown in Figure 7(c)-(d), resulting in amorphous/turbostratic carbon materials. Moreover, the peak intensity of the crystalline impurity also decreases as activation time increases, indicating that at a longer activation time, KOH and the carbonized material thoroughly interacted to reduce the final impurities in the material. It is noteworthy that the carbonization and KOH activation factors have a strong influence on the crystalline structure of the as-prepared samples.

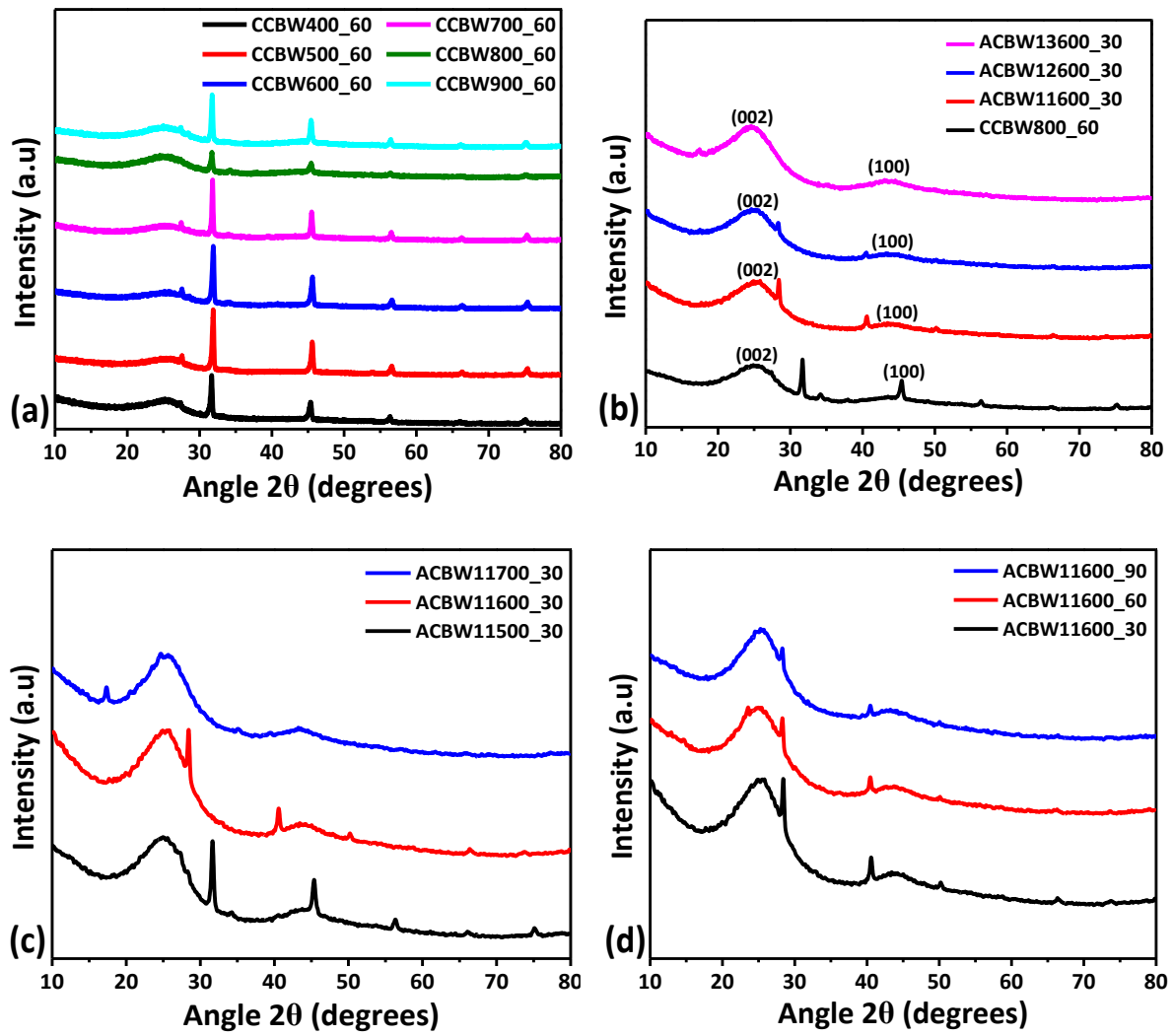


Figure 7: XRD patterns of CCBW and ACBW materials at various (a) carbonization temperatures, (b) activation KOH ratios, (c) temperature, and (d) time.

4.1.1.2 Activated carbon@NiCo₂O₄ nanocomposite

XRD was used to analyze the crystallinity of the electrode materials, and the XRD patterns are shown in Figure 8 (a-c). AC@NiCo₂O₄ samples exhibit diffraction values of $2\theta = 17.3, 33.8, 36.4, 39.5, 47.1, 59.5, 64.9, \text{ and } 79.0^\circ$, which are well identified as the (111), (220), (311), (222), (400), (422), (511), (440), and (533) planes of the spinel cubic structure of NiCo₂O₄, and the results are in good agreement with the literature [32], [146], [147]. The peak intensity corresponding to these planes increased with increasing hydrothermal treatment temperature, time, and urea ratio, indicating enhanced crystallinity of the samples. In addition, all samples showed a characteristic peak at around $2\theta = 12.1^\circ$, which could be attributed to the hkl plane (001) of graphene oxide with attached oxygen-containing functional groups on its basal plane

[148], [149]. This implies that incorporating O atoms into carbon leads to more defects in the carbon framework, as observed in these results [150].

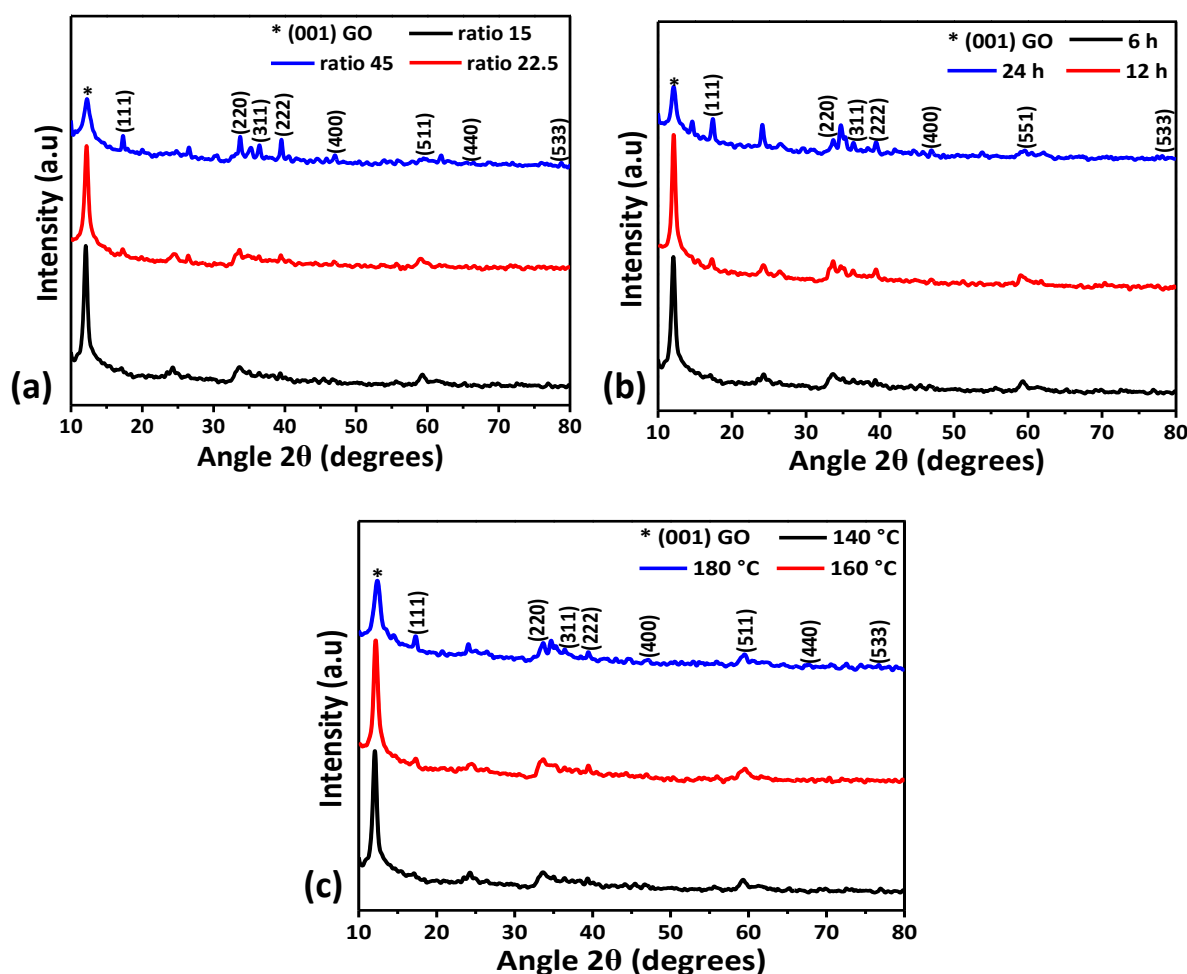


Figure 8: XRD patterns of activated carbon@NiCo₂O₄ composites at different hydrothermal conditions: varying a) urea content b) hydrothermal time and c) temperature.

4.1.2 Fourier-transform infrared spectroscopy (FTIR)

The surface chemistry of activated carbon@NiCo₂O₄ composites prepared under various hydrothermal conditions was investigated further using FT-IR spectroscopy. Figure 9 (a)-(c) depicts the FTIR spectra of all synthesized activated carbon@NiCo₂O₄ composites. Sharp bands at 345.72 and 621.75 cm⁻¹ are attributed to octahedral Ni–O and tetrahedral Co–O vibration stretching [151]–[153]. C–O stretching, N–O stretching, C≡C stretching, and OH stretching are attributed to the characteristic peaks at 1054.35, 1515.76, 2187.45, and 3600 cm⁻¹, respectively (Table 2). Hydroxyl and carbonyl groups interact with the electrolyte ions, inducing pseudo-capacitance [154]. Consequently, the incorporation of pseudo-capacitance can potentially enhance the activated carbon's electrochemical performance.

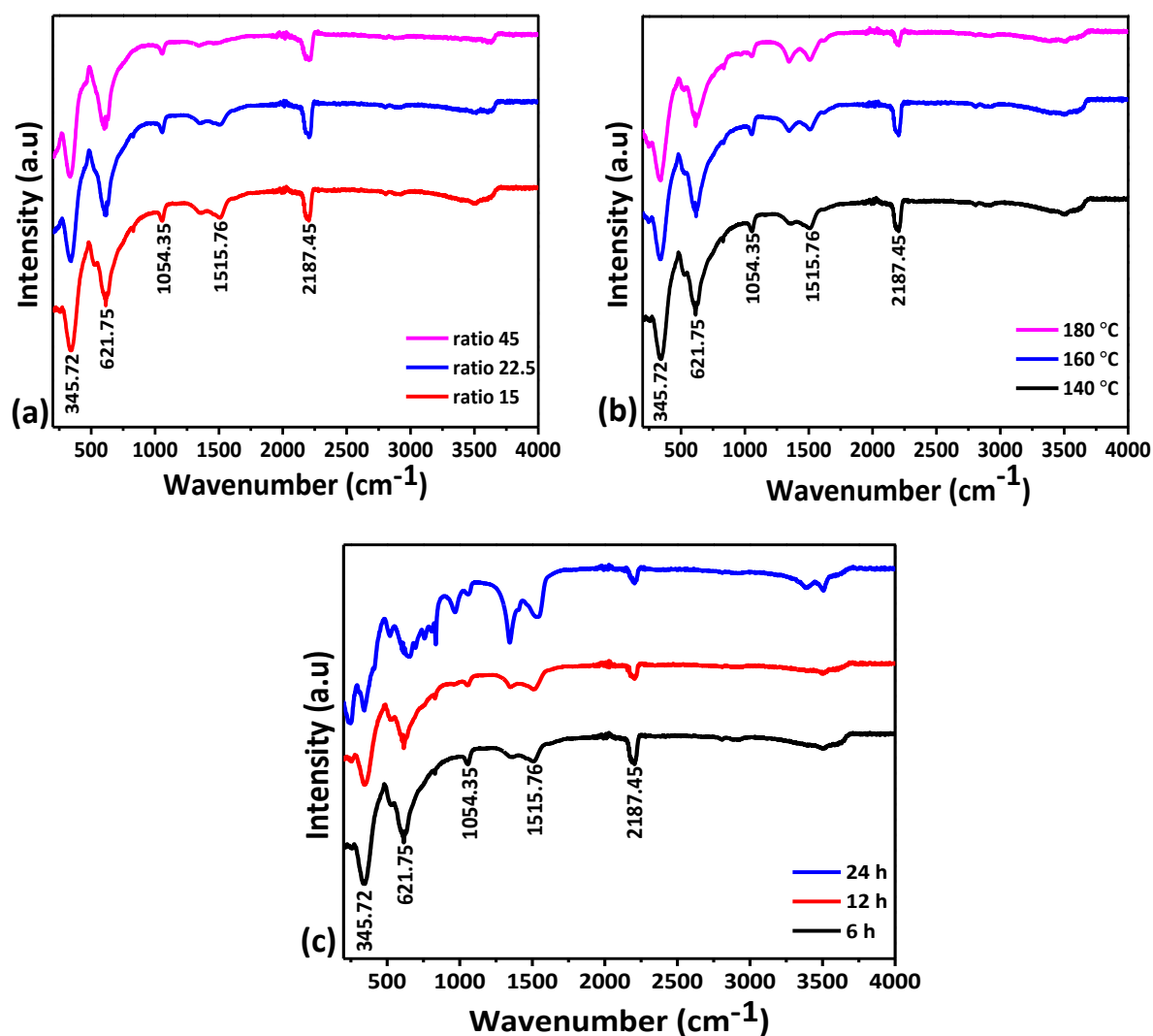


Figure 9: FTIR spectra of activated carbon@NiCo₂O₄ composites at different hydrothermal conditions: varying a) urea content b) hydrothermal time and c) temperature

Table 2: FTIR spectra frequency with possible assignment

Frequency (cm ⁻¹)	Possible Assignment
345.72	Ni-O stretching (Octahedral)
621.75	Co-O stretching (Tetrahedral)
1054.35	C-O stretching
1515.76	N-O stretching
2187.45	C=C stretching
3600	O-H stretching

4.1.3 Raman spectroscopy

Raman scattering is a popular technique used for determining the structural and electronic features of graphitic materials.

The Raman spectra reveal two main peaks at approximately 1343 cm^{-1} conforming to the D band and 1592 cm^{-1} corresponding to the G bands of the carbon materials (Figure 10). The disordered carbon structures with defective site nature give rise to the D-band, whereas graphitic carbon made up of the Sp^2 bonded carbon atoms give rise to the G-band. The I_D/I_G ratio demonstrates both the degree of graphitization and the disordered carbon framework. A high value of I_D/I_G denotes more structural defects within the carbon matrices which, can benefit charge storage in electrochemical devices [155]. Figure 10(a) shows that the intensity ratio increased with increasing carbonisation temperature up to $700\text{ }^\circ\text{C}$ and dropped to 1.04 at $900\text{ }^\circ\text{C}$. When the carbonisation temperature is raised to the graphitization regime, the I_D/I_G decreases because the disordered carbon structures become more oriented and form graphitic domains [156]. Similarly, the intensity ratio increased when the activation temperature was increased up to $600\text{ }^\circ\text{C}$ and then dropped when the temperature was increased to $700\text{ }^\circ\text{C}$ (Figure 10b). This is due to the layer reorganization in the carbon framework caused by the high activation temperature treatment. Increasing activation temperature and time (Figures 10(b) and (c)) led to an increment in the I_D/I_G value, indicating more defects that increase active sites and active surface area of electrode materials for capacitance enhancement [157]. However, excessive defects, on contrary, can obstruct the electrolyte ion diffusion pathway. As the activation KOH ratio increased, (Figure 10d), from 0 to 3, the I_D/I_G ratio decreased from 1.05 to 0.98, indicating that a high activation ratio improved the degree of graphitization by removing defects.

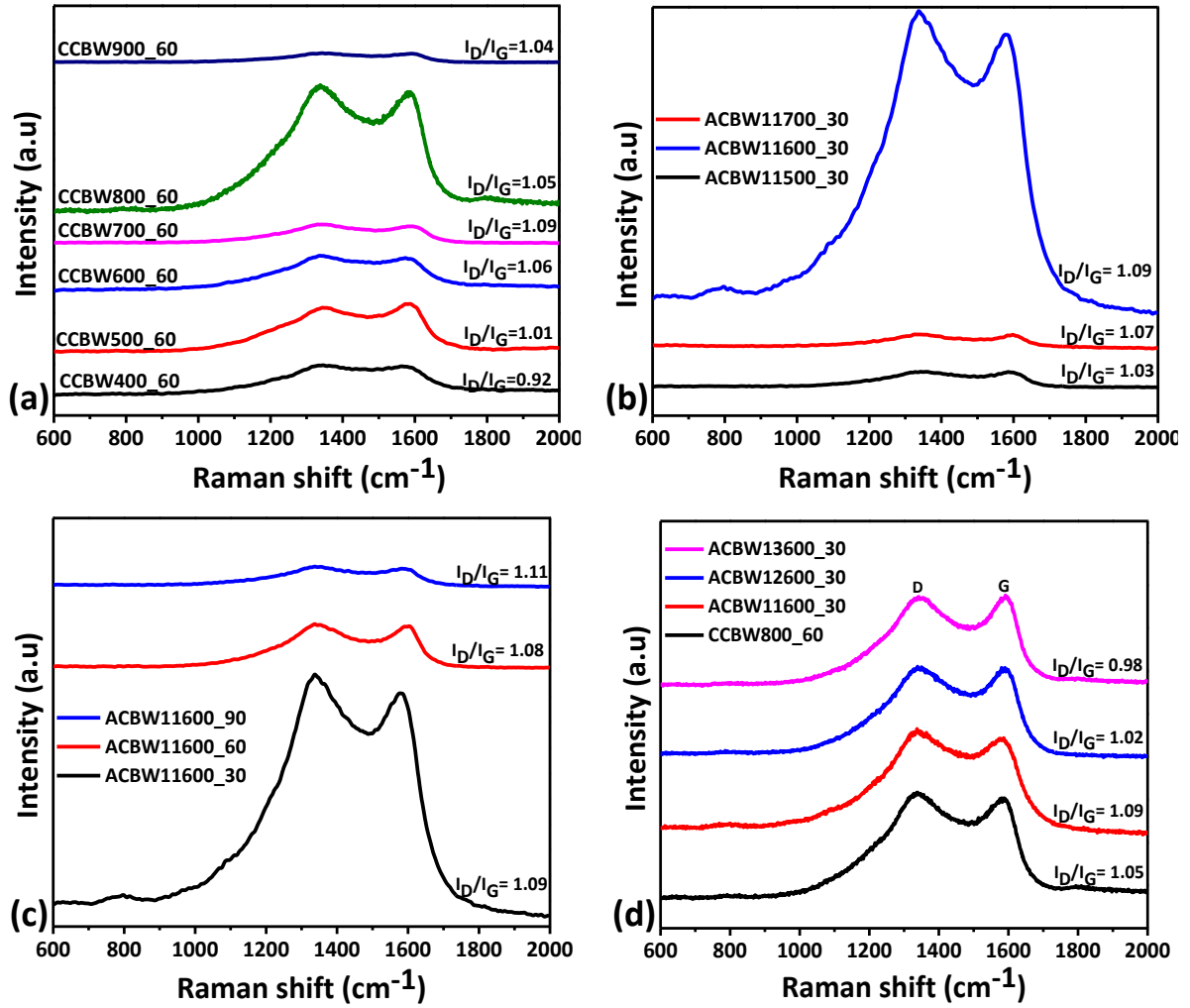


Figure 10: Raman spectra of carbonised and activated materials: varying a) carbonisation temperature, b) activation temperature, c) activation time, and d) activation KOH ratio.

4.1.3.1 Activated carbon@NiCo₂O₄ composite

All samples show peaks at 235, 458, 503, and 652 cm⁻¹, which correspond to the A_{1g}, F_{2g}, E_g, and E_{2g} modes of NiCo₂O₄ and are related to the vibration of Co-O and Ni-O bonds, as shown in Figure 11. These modes are consistent with previously reported values[158], [159]. The D and G bands of activated carbon have vibrational peaks at approximately 1349 and 1591 cm⁻¹, respectively. The D-band is related to structural disorders and defects, whereas the G band is found in all graphitic structures and is commonly associated with the E_{2g} phonon of sp² C atoms, which corresponds to stretching vibrations in the basal plane of single crystal activated carbon. The I_D/I_G ratio, as shown in Figure 10 (a), (b), and (c), increased as urea content, hydrothermal temperature, and time decreased respectively. The higher the intensity ratio the more defects and disorders on the activated carbon surface due to the existence of NiCo₂O₄.

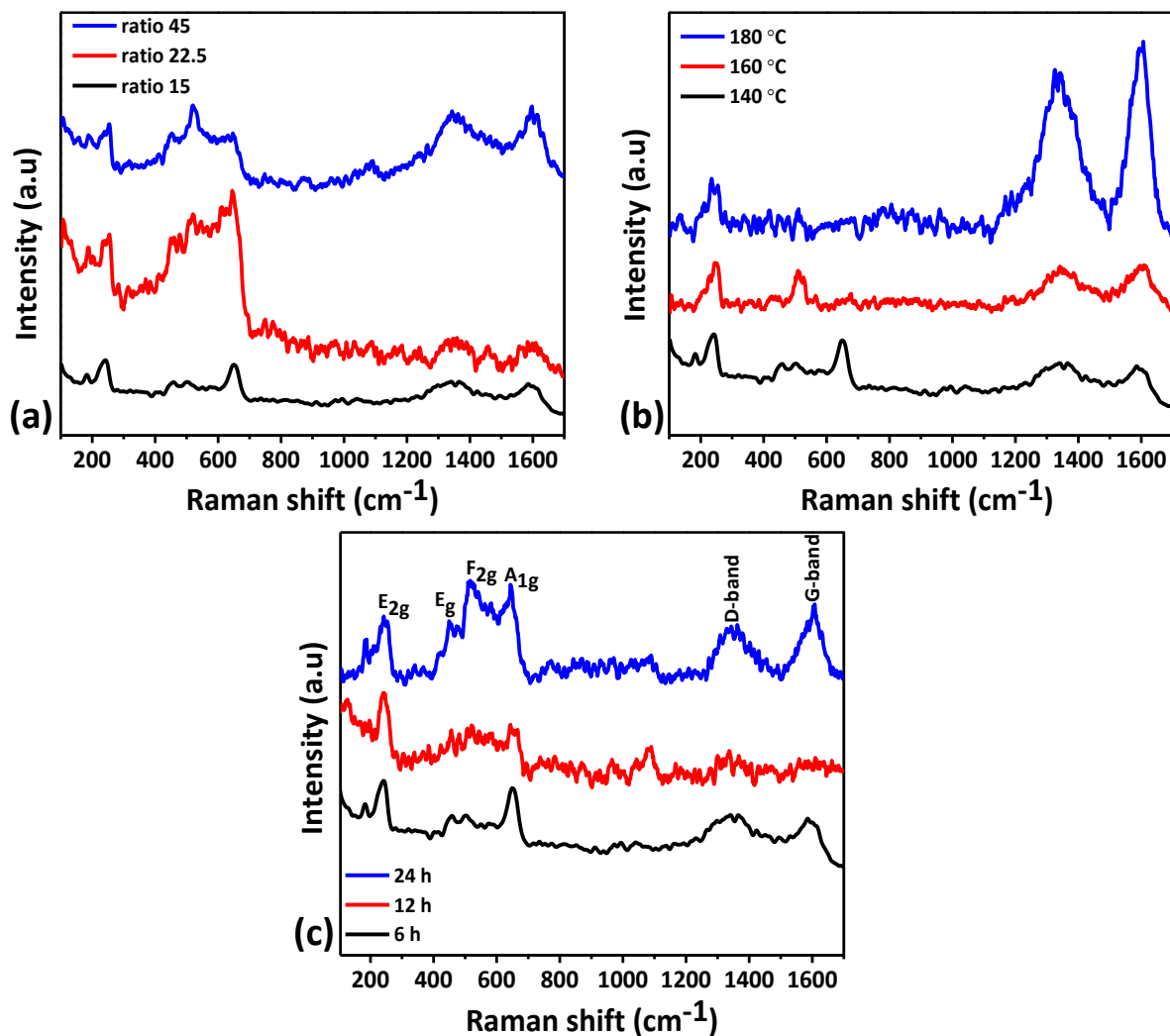


Figure 11: Raman spectra for activated carbon@NiCo₂O₄ composites at different hydrothermal conditions: varying a) urea content b) hydrothermal time and c) temperature

4.1.4 Nitrogen BET adsorption-desorption

At 77.35 K, the porosity and surface area of all produced samples were investigated using the N₂ desorption-adsorption isotherm method. ACBW11600_30 material exhibited a type IV isotherm between 0.2 and 1.0 relative pressure [73] with H₄ hysteresis as shown in Figure 12(a), indicating pores forming slit-shaped arrangement, which is typical of microporous materials. However, the remaining samples show type I isotherms, suggesting that they are microporous. Table 3, shows that the non-activated CCBW sample had the smallest BET surface area, micropore volume, micropore surface area, and total pore volume, which may account for its poor capacitive behaviour. The BET surface areas of CCBW800_90, ACBW11600_30, ACBW12600_30, and ACBW13600_30 was 26, 320, 206, and 136 m² g⁻¹, respectively (Table 3). When CCBW/KOH activation ratio was increased to 3, the total pore volume and specific surface area decreased. The decrease in BET-specific surface area can be attributed to a

reduction in microporous volume caused by high KOH on the carbon surface, which disrupts the microporous structure. In general, carbon activation with KOH gives K_2CO_3 at temperatures around 400 °C (Eq.6). At temperatures above 700 °C, K_2CO_3 is considerably decomposed to K_2O and CO_2 (Eq.7) and fully decomposed at 800 °C. Furthermore, as shown in Eq. 8, the resulting CO_2 is reduced to CO by carbon. K compounds such as K_2CO_3 and K_2O are also reduced by carbon at temperatures above 700 °C, resulting in metallic K. (Eq. 9 and 10). Equations 6-10 illustrate the mechanisms of KOH activation [161]:



The maximum specific area for the ACBW11600_30 sample was 320.73 m² g⁻¹, which is 91.9% larger than CCBW800_60. The decomposition of K_2CO_3 at around 600 °C may have resulted in the formation of microporous structures in carbon materials, increasing the specific surface area and total pore volume.

The carbonized material, CCBW800_60, displayed a virtually flat pore size distribution curve with a slight hump at 4 nm and an extremely low pore volume, as shown in Figure 12(b). This, combined with the absence of a hysteresis loop (Figure 12a), indicates that the sample is non-porous. Micropores (pore sizes of 2 nm or less) and mesopores (2 – 13.5 nm) are present in all the samples, as shown in Figure 12(b) [74]. Figure 12b shows a strong pore distribution peak concentrating at around 1.17 nm and a high increment pore volume at activation ratio 1 (ACBW11700_30), which agrees with the pronounced broad hysteresis loop in Figure 12a, indicating that the sample contained many micropores. When the activation KOH ratio was increased to 2 and 3, the pore size distribution remained centered at 1.17 nm, but there was a significant change in increment pore volume, Figure 12(b). The decrease in the pore volume with an increase in the activation ratio indicates a loss of microporosity in the carbon.

Figure 12(c) depicts cumulative pore volume curves of all materials. The intercalation of potassium onto the carbon surface caused by the addition of the KOH activating agent resulted in the formation of additional pores [163]. When the KOH ratio was 1, pore volume increased to 0.19 cm³ g⁻¹, increasing KOH to 2 and 3, pore volume decreased to 0.12 and 0.08 cm³ g⁻¹, respectively. The significant cumulative pore volume is due to both mesopores and micropores [75]. The existence of micropores and mesopores on the external surface enables ion storage

and provides defined diffusion pathways for electrolytes to access the electrode materials, both of which are critical in practical supercapacitor technologies.

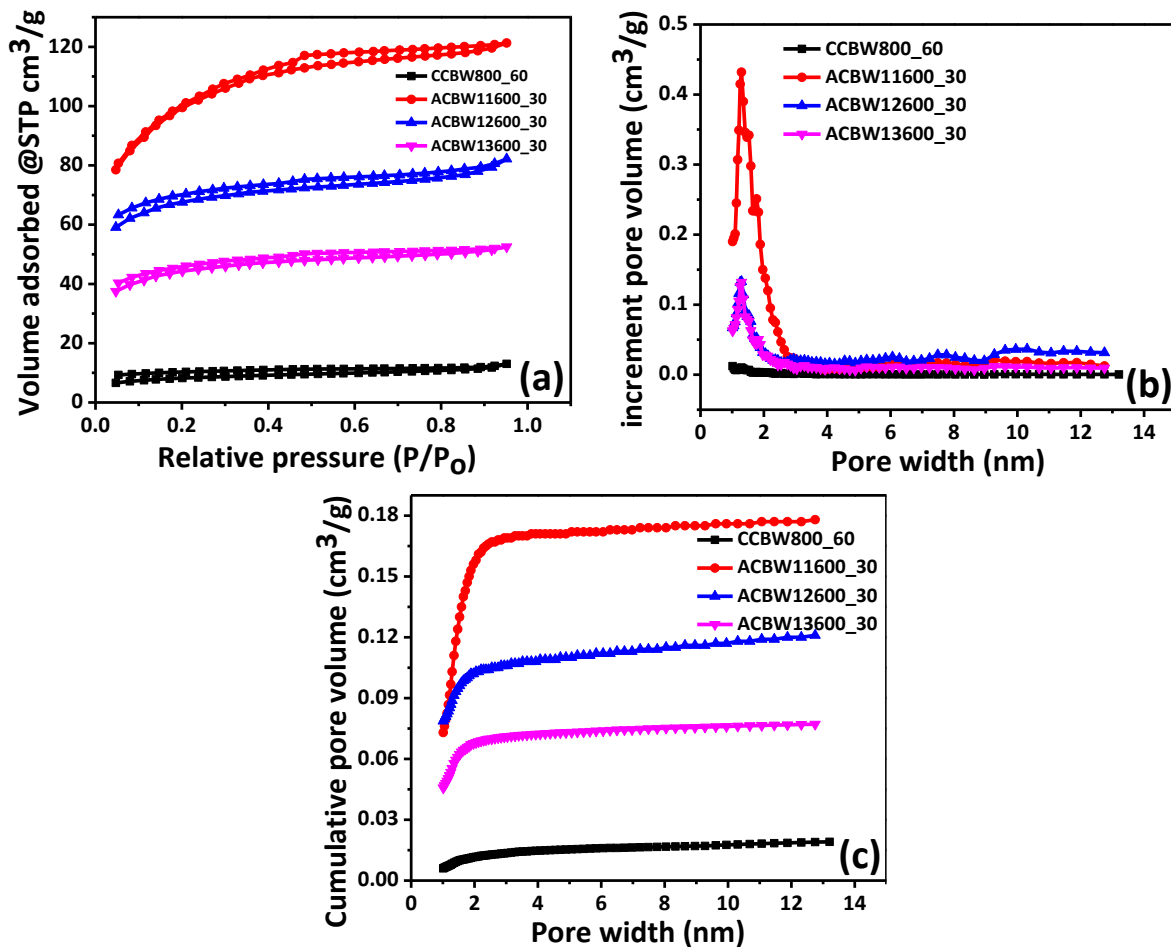


Figure 12: a) N₂ BET sorption isotherm, b) pore size distribution and c) cumulative pore volume profiles for CCBW800_60, ACBW11600_30, ACBW12600_30 and ACBW13600_30.

Table 3: Specific surface area and pore characteristics.

Samples	¹ S _{BET} (m ² g ⁻¹)	² V _{total} (cm ³ g ⁻¹)	³ V _{micro} (cm ³ g ⁻¹)	⁴ D _{ave} (nm)	⁵ S _{ext} (m ² g ⁻¹)	⁶ S _{micro} (m ² g ⁻¹)
CCBW80060	26.1	0.020	0.008	1.55	10.22	15.91
ACBW1160030	321	0.188	0.091	1.17	145.67	175.06
ACBW1260030	207	0.128	0.082	1.23	52.63	154.25

ACBW1360030	137	0.081	0.052	1.19	38.16	98.16
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¹=BET surface area, ²=total pore volume, ³=vt method micropore volume, ⁴=average pore size, ⁵=external surface area, ⁶=vt micropore surface area.

4.1.5 Scanning and Transmission Electron Microscopy

The surface texture of the materials produced was investigated using a scanning electron microscope (SEM), as shown in Figure 13(a)-(d). Carbon with block-like structures on the surface was generated following carbonization at 800 °C (Figure 13a). As shown in Figure 13e, flakes/rods are present, which could be because of iron, silicon, and other contaminants in the sample, possibly from the detergents used to clean the slaughterhouse floor. This is supported by the presence of impurity peaks in the XRD patterns, Figure 7(a). When KOH was added to the carbonised material, the rods or flakes-like morphology disappears (see Figures 13(b)–(d) and (f)–(h). Increasing the KOH activation ratio from 1 to 3 resulted in the formation of additional pores. XRD analysis shows that increasing the KOH activation ratio from 1 to 3 etches away impurities. Furthermore, the morphological and structural changes in activated carbon were investigated by TEM. When compared to its activated counterparts, the carbonized sample (Figures 14(a) and (e) had worm-like edges, which are characteristic of heterogeneous amorphous carbon, and densely packed particles that were relatively small and thick (Figures 14(b)–(c) and (f)–(g). At KOH activation ratio 1, the surface of the samples is thinner, indicating a more carbonaceous material (Figure 14f). When the KOH ratio is increased to 2, the sample has a smaller and straight line-like morphology, indicating the presence of metal oxides, specifically iron, and the loss of its carbonaceous nature. The carbon structure burns away as the KOH ratio approaches 3, favoring the KOH ratio 1 because it contains more carbon. Furthermore, due to weak Van der Waals forces, all iron impurities were removed at ratio 3, causing the carbon layer to re-stack and form a thick layer. As a result, the surface area and pore volume may be reduced. At KOH ratio 1, the TEM results demonstrate carbon with high porosity, which is consistent with N₂ sorption investigations, which provide the biggest hysteresis loop and a strong pore size distribution peak centered about 1.17 nm with the maximum pore volume for activated carbon materials..

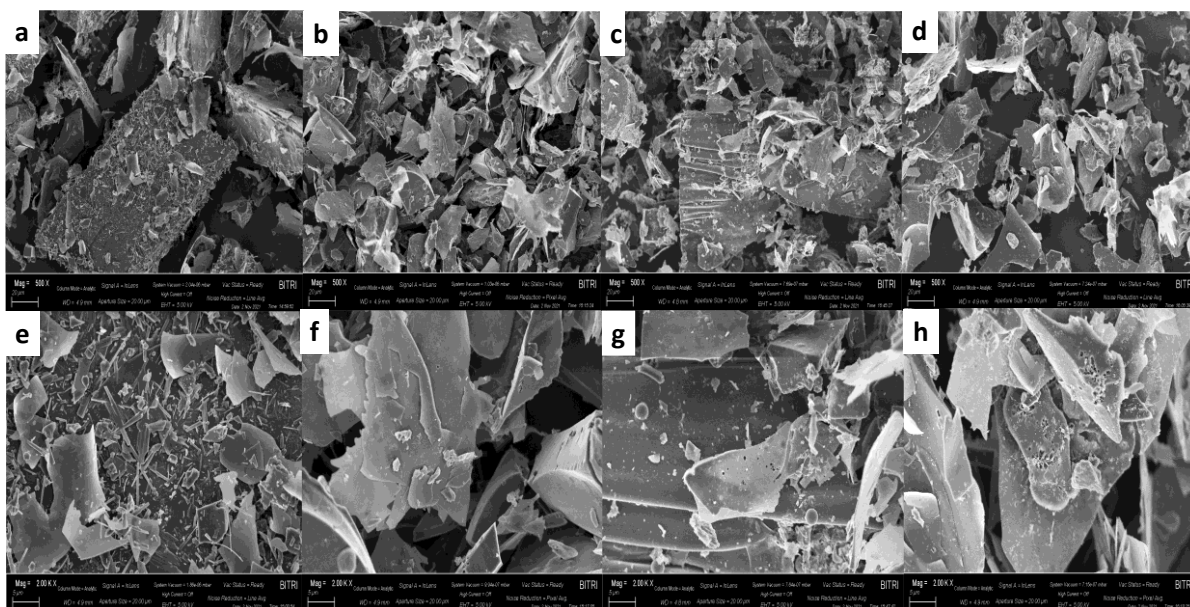


Figure 13: (a–d) Low magnification (x500) SEM images of CCBW800_60, ACBW11600_30, ACBW1200_30, and ACBW13600_30, respectively, and high magnification (x20 000) SEM images of (e–h).

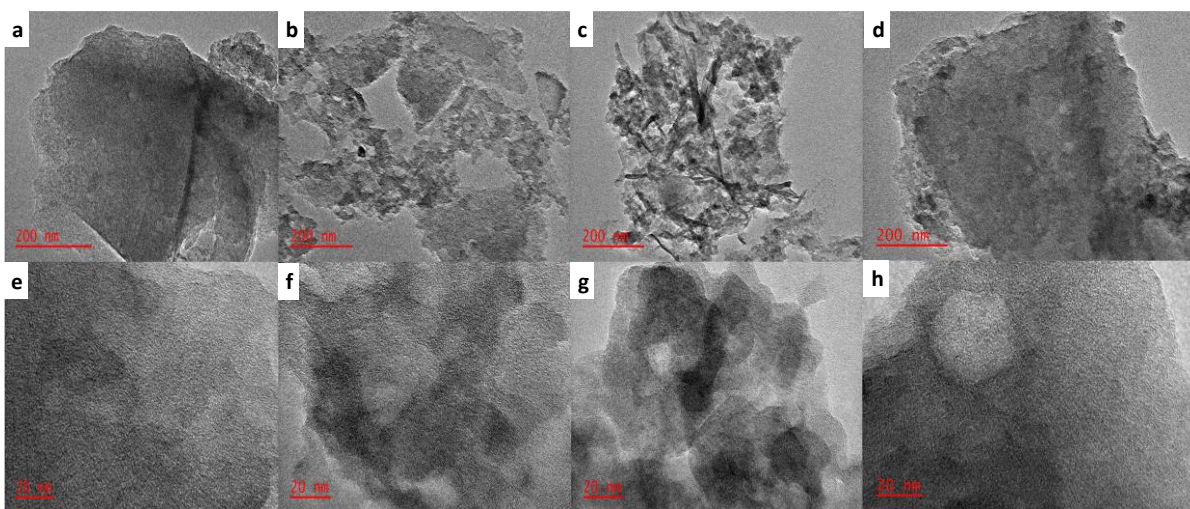


Figure 14: (a–d) low magnification TEM images of CCBW800_60, ACBW11600_30, ACBW1200_30, and ACBW13600_30, in that order; (e–h) high magnification TEM images of (a–d).

4.1.6 Thermogravimetric analysis

Thermal gravimetric analysis (TGA) was used to determine the materials' thermal stability, and the results are shown in Figure 15. The thermograms of all samples show an initial mass loss of 10% at 100 °C due to the evaporation of moisture from the materials [165]. Beyond 400 °C, the second weight loss rate for all activated carbon samples increased with increased

activation KOH ratio, indicating a breakdown of low-stability surface functional groups formed during activation and degradation of the organic carbon skeleton [166]. These functional groups can be more susceptible to oxidation or other chemical reactions at high temperatures [167], leading to weight loss and decreased thermal stability of activated carbon materials between 400 and 900 °C, compared to carbonised samples. However, the phase transition of iron caused the mass loss between 490 and 570 °C [168], which resulted in the sample activated at a KOH ratio of 1 exhibiting less mass loss, indicating that it is more stable. At ratios 1:2 and 1:3 the activated carbons have identical thermal properties. The last weight loss of 10% over 600 °C could be ascribed to the degradation of inorganic materials and the reduction of iron oxide in ash by carbon [169]. Thus, the oxygen in iron oxide reacted with the carbon in the residue to generate CO and CO₂.

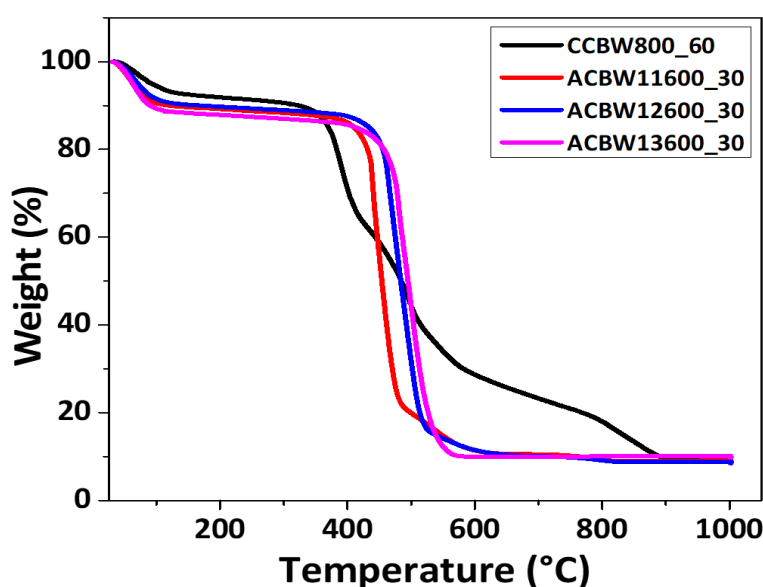


Figure 15: TGA profiles for carbonised and activated carbon samples

4.2 Electrochemical Tests – Three Electrode System

Cyclic voltammetry, cyclic charge-discharge, electrochemical impedance spectroscopy, and stability measurements were performed using a three-electrode system in a 6 M KOH solution to determine the electrochemical behavior of the prepared working electrodes.

4.2.1 Cyclic Voltammetry (CV)

4.2.1.1 CVs for Activated Carbon Materials

Figure 16 (a)-(d) depicts cyclic voltammograms of electrode materials made from CCBW and ACBW samples at 100 mV s⁻¹ sweeping rate. All the CCBW and ACBW materials have a relatively regular rectangular shape, as shown in Figure 16, indicating their desirable EDL

capacitance behaviour. As is common in CV, a voltage is applied and the resulting current is measured, which is then used to compute the capacitance equation. Thus, the output current determines the specific capacitance. A great current response was observed with increasing carbonisation temperature and time, Figures 16(a) and 16(d). Figure 16(b) shows that increasing an activation KOH ratio from 0 to 3 resulted in a decrease in the current response and area under the CV curve. Similarly, increasing the activation temperature from 600 to 700 °C decreased the current response and area under the CV curve. This suggests that high activation KOH ratios and temperatures degrade the microstructure of the carbon material, which leads to lower specific capacitances. When compared to CCBW and other ACBW samples at 100 mV s^{-1} , the electrode prepared from ACBW11600_30 had a large area under the CV curves, indicating high specific capacitance. Figure 16(e) shows the cyclic voltammograms of ACBW11600_30 electrode materials at various sweeping rates. All the curves maintained a similar shape at 5, 10, 20, and 50 mV s^{-1} , indicating that the electrodes demonstrate cation diffusion and rapid charge transfer between the electrolyte solution and electrode material, thereby producing more active sites.

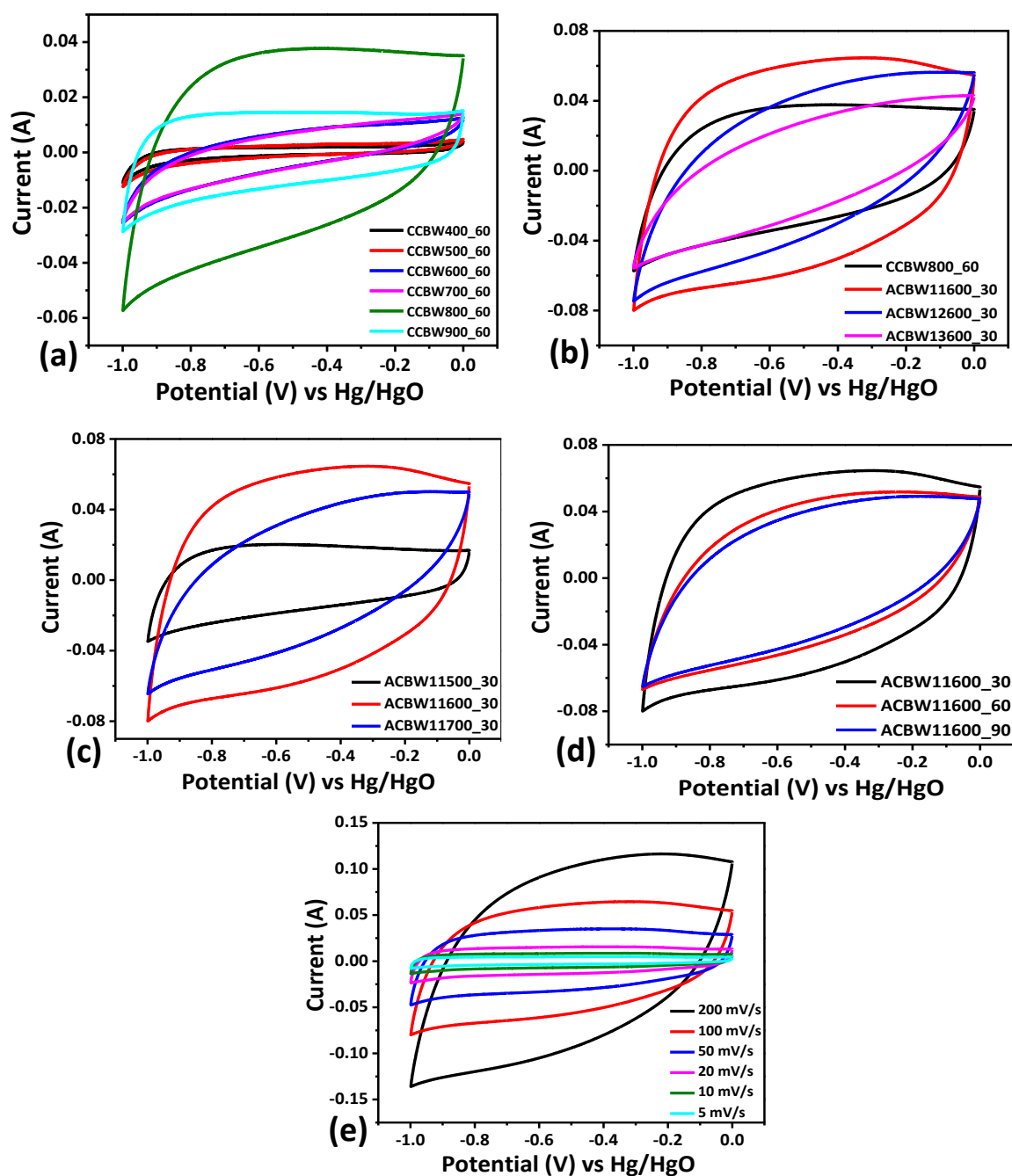


Figure 16: Cyclic voltammograms of electrodes prepared from samples (a) carbonised at different temperatures, activated at different (b) activation temperatures, (c) time, and (d) KOH ratio at 100 mVs^{-1} in three-electrode and (e) ACBW11600_30 sample at varied scanning rates.

4.2.1.2 CVs for Activated carbon@NiCo₂O₄ Composite

Cyclic voltammograms of AC@NiCo₂O₄ materials prepared under various hydrothermal treatment conditions in the voltage window from 0.15 to 0.55 V are shown in Figure 17 (a)-(e). All cyclic voltammograms show a distinct pair of redox peaks, confirming the pseudocapacitive behaviour of AC@NiCo₂O₄ materials. Reversible redox peaks are observed

at 0.3 V (cathodic peak) and 0.44 V (anodic peak) for each electrode, which is attributed to faradaic redox reactions, which are particularly associated with the phases of $\text{Ni}^{2+}/\text{Ni}^{3+}$, $\text{Co}^{2+}/\text{Co}^{3+}$, and $\text{Co}^{3+}/\text{Co}^{4+}$ redox couples for NiCo_2O_4 , as described by the following equations 11-13 [170], [171].

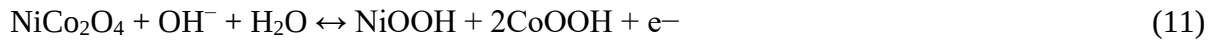


Figure 17(a) shows that the area under the CV curve was larger at 15 mmol urea ratio than at 22.5 and 45 mmol, indicating better capacitance at lower nitrogen content. Doping carbon with nitrogen with urea as a precursor aided in the optimization of the structure of NiCo_2O_4 and resulted in fast electron transfer. The CV curves for $\text{AC}@\text{NiCo}_2\text{O}_4$ electrodes prepared at 140 and 180 °C have almost the same area, indicating that increasing hydrothermal temperature did not improve capacitance, Figure 17(b). As hydrothermal time increased from 6 to 24 h, the area under the CV curve decreased as shown in Figure 17(c). Figure 17(d) shows that as the carbon loading mass increased to ($\text{NiCo}_2\text{O}_4\text{:AC}$) 1:2 and 1:3, the cathodic peak transitioned from 0.3 V to 0.35 V, which is attributed to the polarization of the electrode material [172]. Additionally, the electrode materials' area under the CV curve decreases at a scan rate of 5 mV s^{-1} , indicating a decrease in specific capacitances. When the mass ratio exceeds 1:1, activated carbon becomes a constraint, allowing less charge to be stored. The peak current density of $\text{NiCo}_2\text{O}_4\text{:AC}$ (1:0.5) is the highest of all the CV curves, which may account for the higher specific capacitance. This is influenced by the redox reactions of NiCo_2O_4 that lead to a change in the valence electrons of $\text{Co}^{3+}/\text{Co}^{4+}$ and $\text{M}^{2+}/\text{M}^{3+}$ ($\text{M} = \text{Co}$ or Ni) on the surface of the composite electrode, increasing the reversibility of the Faradaic reaction process [31]. Greater redox potential elements, such as Co^{3+} , result in ion transfer through the Faradaic process and oxidation of Co^{4+} elements in $\text{AC}@\text{NiCo}_2\text{O}_4$. Contrarily, activated carbon's enormous specific surface area can efficiently accommodate NiCo_2O_4 and offer structural support to prevent the agglomeration of the metal oxide [171]. Additionally, carbon facilitates the composite's wettability and electrical conductivity [173].

Figure 17(e) shows the CV curves at different scan rates for the electrode material prepared under optimal hydrothermal conditions (15 mmol urea ratio, 140 °C, 6 h, 1:0.5). The peak current increases as the scan rate increases, revealing that the charge-discharge step is

reversible [174]. Furthermore, the anodic and cathodic peaks shift towards the higher and lower potential region as the scan rate increases. This is because the charge transport rate during the redox reaction is satisfying the electronic stabilisation or polarization [175]. The CV curves' shape can be well retained at different scan rates, demonstrating the materials' great stability and fast mass transfer rate.

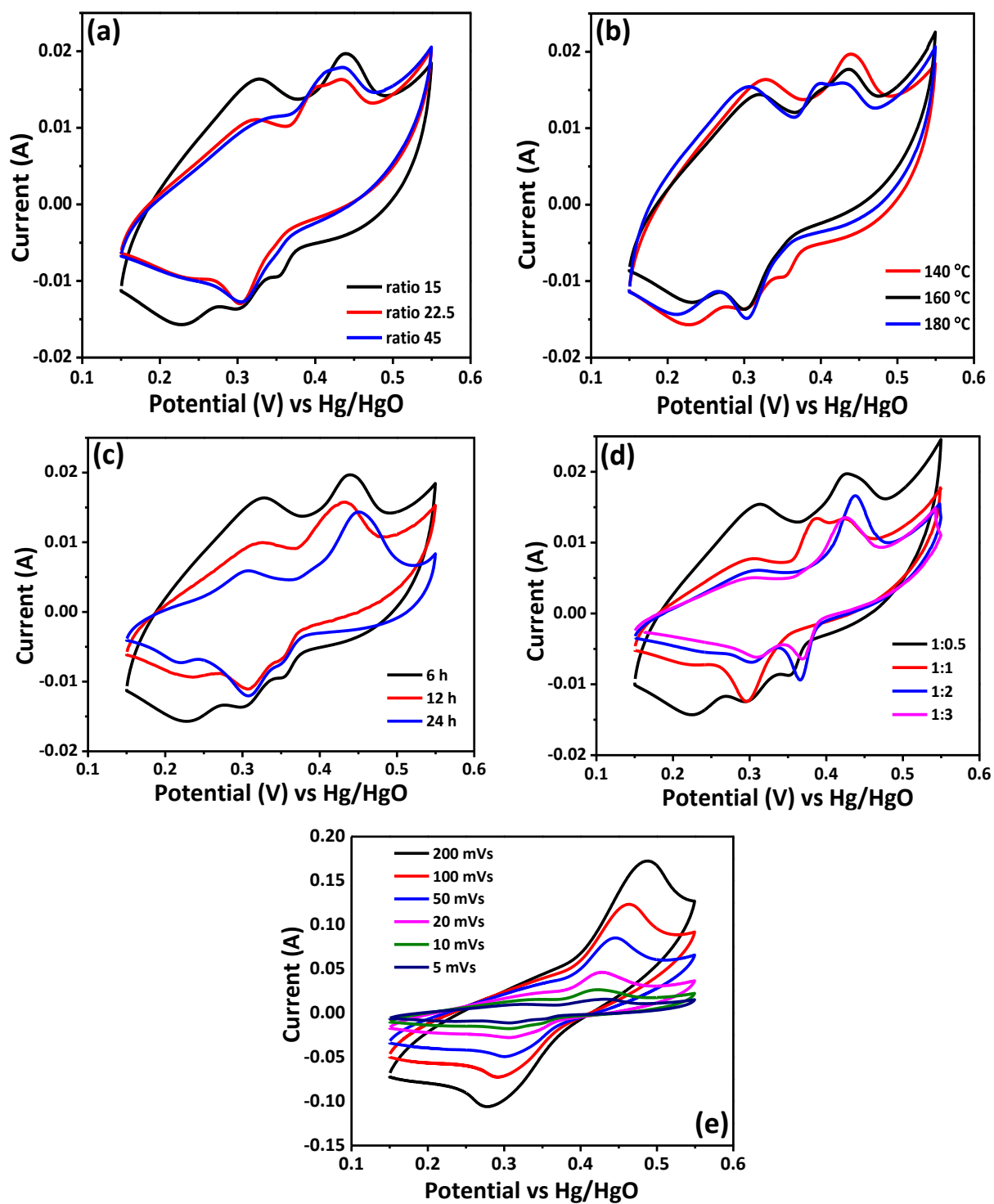


Figure 17: Cyclic voltammograms of (a-c) AC@NiCo₂O₄ at varied hydrothermal treatment conditions at 5 mV s⁻¹ d) NiCo₂O₄: different carbon mass loading at 1:0.5, 1:1, 1:2, and 1:3, correspondingly at 5 mVs⁻¹ and e) NiCo₂O₄/AC (1:0.5) at various scanning rates.

4.2.2 Cyclic Charge Discharge (CCD)

4.2.2.1 CCD for Activated Carbon Materials

Figure 18(a)-(d) depicts cyclic charge-discharge (CCD) curves for all electrode materials at current density of 0.5 A g^{-1} and a working voltage window that ranges from 0 to -1V. The CCD curves, as shown in Figure 18(a)-(e), for all samples have almost symmetrical triangular shapes and small potential IR drop, signifying high electrochemical reversibility, good coulombic efficiency, and low electrode internal resistance [176]. Figure 18(a) depicts that the electrode materials carbonized at temperatures below and above 800°C had a shorter charge-discharge time than the CCBW800_60 electrodes. This indicates that at higher carbonisation temperatures (up to 800°C), the specific capacitance increased, whereas, at higher temperatures (900°C), it decreased. It is noteworthy that the charge-discharge time for the ACBW11600_30 electrodes is longer than that for the ACBW12600_30 and ACBW13600_30, demonstrating that the capacitance increased with a decrease in activation KOH ratios, Figure 18(b). Large BET surface area and micropores, which offered the electrolyte ions with more active sites and rapid electrolyte diffusion, respectively, are responsible for its remarkable performance. [177]. Additionally, the discharging time of the electrodes surpasses the charging time, suggesting a substantial contribution from the pseudo-capacitive behavior. Furthermore, there was a drop in charge-discharge time when the activation temperature was increased to 700°C , Figure 18 (c). Figure 18(d) shows that activation times of 60 and 90 min, have almost the same charge-discharge time, thus increasing activation time did not result in a significant change in the charge-discharge time. However, the total charge-discharge time of ACBW11600_30 is longer than the same electrode at 60 and 90 min, therefore, the optimal charge-discharge time is 30 min. The specific capacitance is directly proportional to the discharge time under constant current, mass (or area), and change in potential. Cyclic charge-discharge curves of ACBW11600_30 from 0.5 to 5 A g^{-1} are depicted in Figure 18(e). The discharge time gradually decreased as current density increased, possibly because electrolyte ions had little time to enter and permeate the porosity of carbon materials [178].

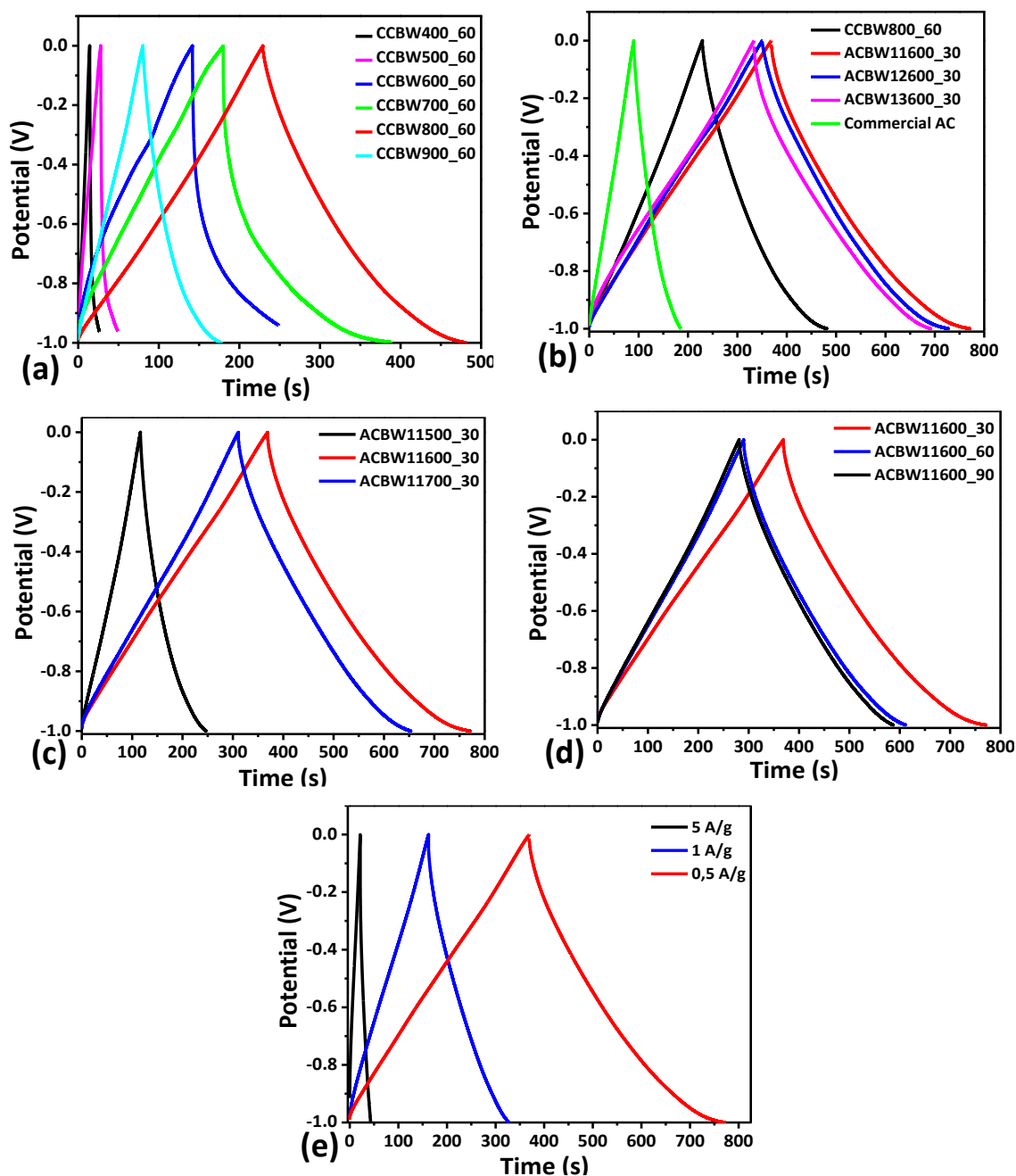


Figure 18: Cyclic charge-discharge curves of (a) CCBW samples prepared at different carbonisation temperatures, and ACBW samples prepared at various activation (b) KOH ratio compared to commercial AC, (c) temperature, and (d) time, at 0.5 A g^{-1} and (e) ACBW11600_30 sample at different current densities, in a three-electrode system.

4.2.2.2 CCD for Activated Carbon@NiCo₂O₄ Composite

Cyclic charge-discharge (CCD) tests were carried out to evaluate the charge storage and rate capability of ACx@NiCo₂O₄ samples and the results are shown in Figure 19. Figures 19(a)-(d) compare CCD curves at 0.5 A g^{-1} current density at voltage windows varying from 0.15 to 0.5 V. All samples exhibit a similar asymmetric curve nature, with differing charging and

discharging times. The charge-discharge time decreased with an increase in urea ratio, hydrothermal time, and carbon mass loading. At a hydrothermal temperature of 140 and 180 °C, the samples have nearly the same charge-discharge time. The longest discharge time was obtained for AC@NiCo₂O₄ prepared at a hydrothermal temperature of 140 °C, time of 6 h, and urea amount of 15 mmol, implying a significantly higher specific capacitance. Nitrogen doping (N-doping) increases the intrinsic activity of each site of the metallic oxides by increasing electronic conductivity [179]. N-doping also reduces electron transport energy, which improves reaction kinetics and promotes redox reaction for high ion mobility [180], [181]. These findings show that at the electrode surface, the electrolyte ions intercalate into nickel cobaltite in an ultra-fast reaction, which contributes to high performance.

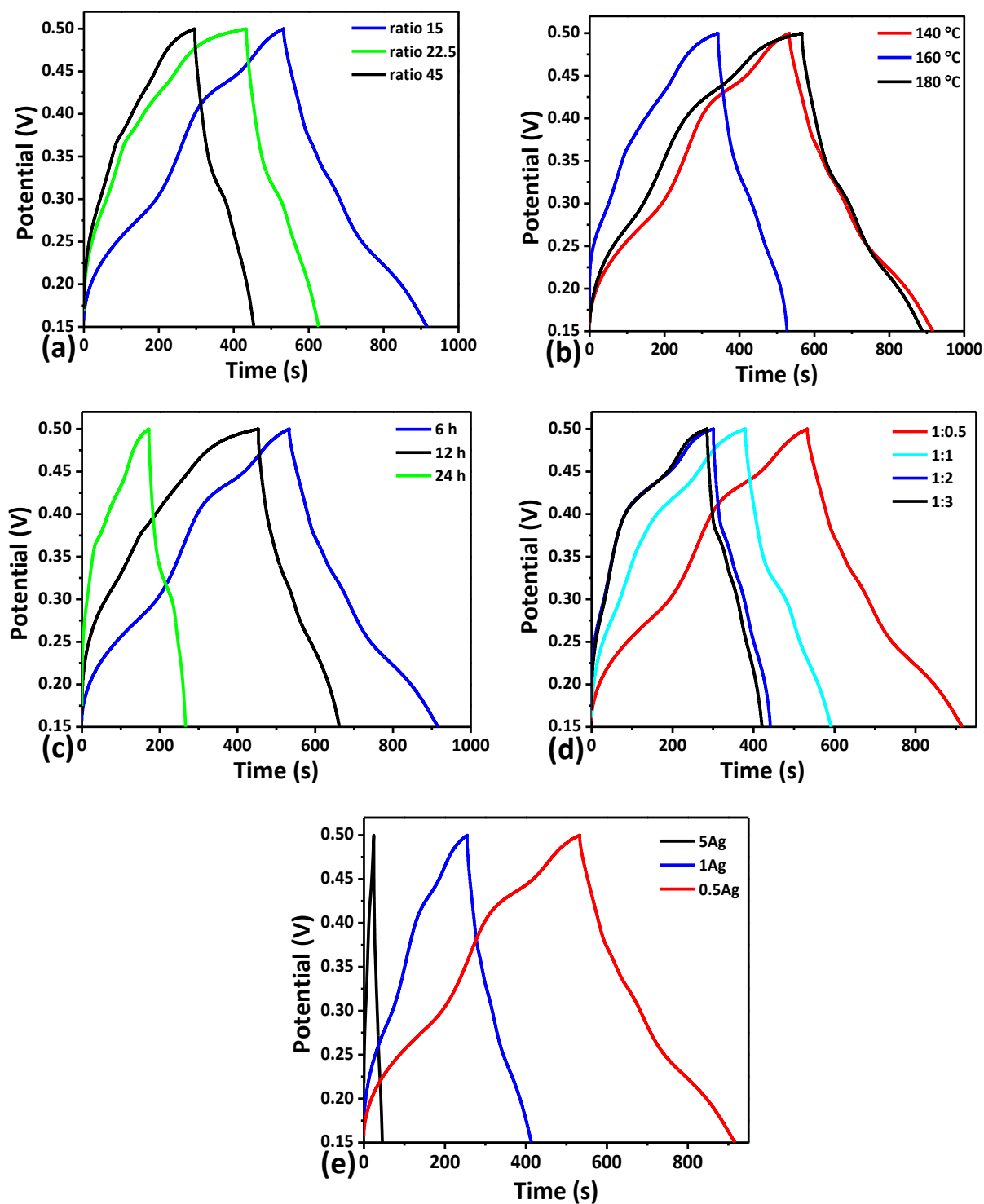


Figure 19: Cyclic charge-discharge of (a-c) AC@NiCo₂O₄ at different hydrothermal treatment conditions at 0.5 A g⁻¹ d) NiCo₂O₄: different carbon mass loading at 1:0.5, 1:1, 1:2 and 1:3, correspondingly at 0.5 A g⁻¹ and e) NiCo₂O₄/AC (1:0.5) at different current densities.

4.2.3 Specific Capacitances for Activated Carbon Materials computed from CV and CCD curves

The specific capacitances of CCBW and ACBW electrode materials at various scan rates and current densities are shown in Figures 20, 21, and 22.

4.2.3.1 Effects of Carbonisation factor on Specific Capacitances

It is worth noting that specific capacitances increased as carbonisation temperature and time increased. However, at the maximum carbonisation temperature of 900 °C, the specific capacitance decreased dramatically as shown in Figure 20 (a)-(b). Similarly, Figure 21(a)-(b) shows that increasing the carbonisation time to 90 min resulted in a decrease in specific capacitances. A sample carbonised at 800 °C for 60 min afforded the highest specific capacitance of 107 and 127 F g⁻¹ at 5 mV s⁻¹ and 0.5 A g⁻¹, respectively. At high carbonisation temperature (800 °C) micropores were formed with average pore size of 1.55 nm, allowing electrolyte ions to easily reach the electrode's outer layer.

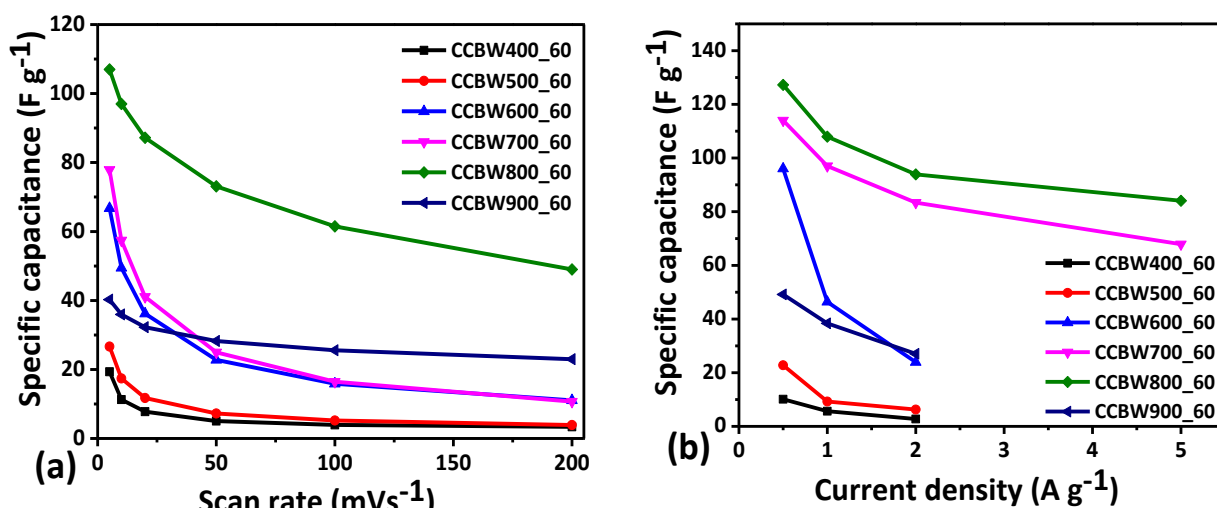


Figure 20: Specific capacitances of CCBW samples prepared at different carbonisation temperatures at (a) various scan rates and (b) current densities

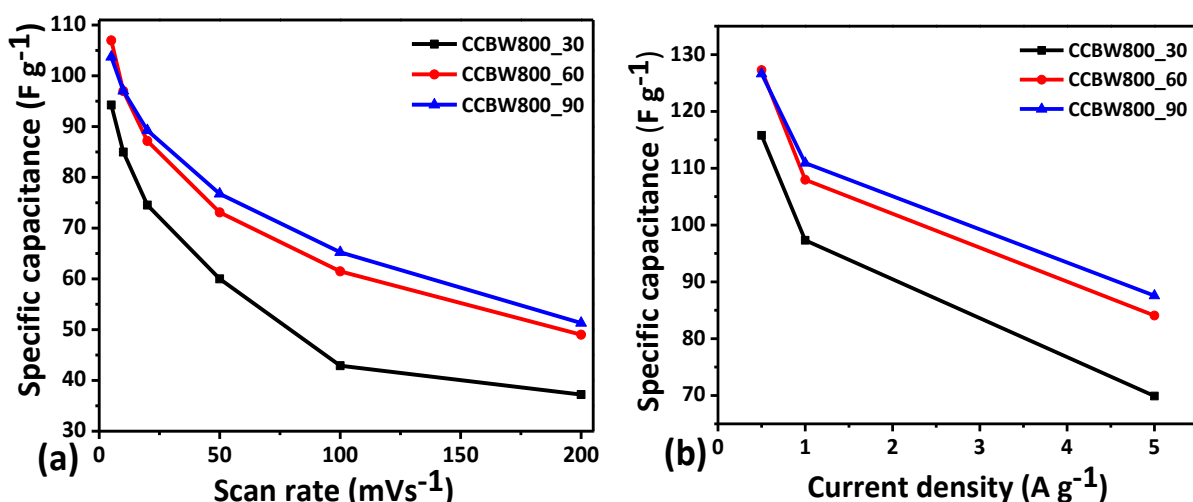


Figure 21: Specific capacitances of CCBW samples prepared at different carbonisation times at (a) various scan rates and (b) current densities

4.2.3.2 Influence of KOH Ratio, Temperature, and Time on Specific Capacitances

Generally, increasing the KOH ratio induce porosity, and increases the surface area in the carbon structure leading to high electrochemical performance. However, it does not seem the case in our work. The BET revealed that the 1:1 KOH ratio sample had the largest surface area, highest total pore volume, and more micropores than the other samples. As a result, the sample prepared following activation conditions; KOH ratio 1, 600 °C, and 30 min (ACBW11600_30) showed the highest specific capacitance of 163 F g^{-1} at 5 mV s^{-1} and 204 F g^{-1} at 0.5 A g^{-1} in the three-electrode system, Figures 21(a) and 22(a). This indicates that ACBW11600_30 is the best option for highly effective supercapacitor applications, in which the kinetics of ion and electron transport is facilitated at the electrode-electrolyte interface [182]. This is due to the free and rapid access of micropores and mesopores by the electrolyte ions. Figures 21(b) and 22(b) show that as activation temperature increased from 500-600 °C, specific capacitance increased significantly. However, a decrease in capacitance was observed when the activation temperature was increased to 700 °C, indicating the deformation of microstructure at high temperatures. Increasing the activation time from 30 to 90 min did not improve the specific capacitance as shown in Figures 21(c) and 22(c).

The specific capacitance of all electrode materials was greater at a low sweep rate, as shown in Figures 21(a)-(c), because of complete interaction of electrolyte ions with the inside part of the working electrode [183]. When the scan rate is increased, the electrolyte ions inadequately interact with the electrode material, lowering the active materials' capacitance. Furthermore, as current densities increased, the specific capacitances of the electrodes (Figures 22a-c) decreased due to insufficient time for ions to access and interact with the electrode [112].

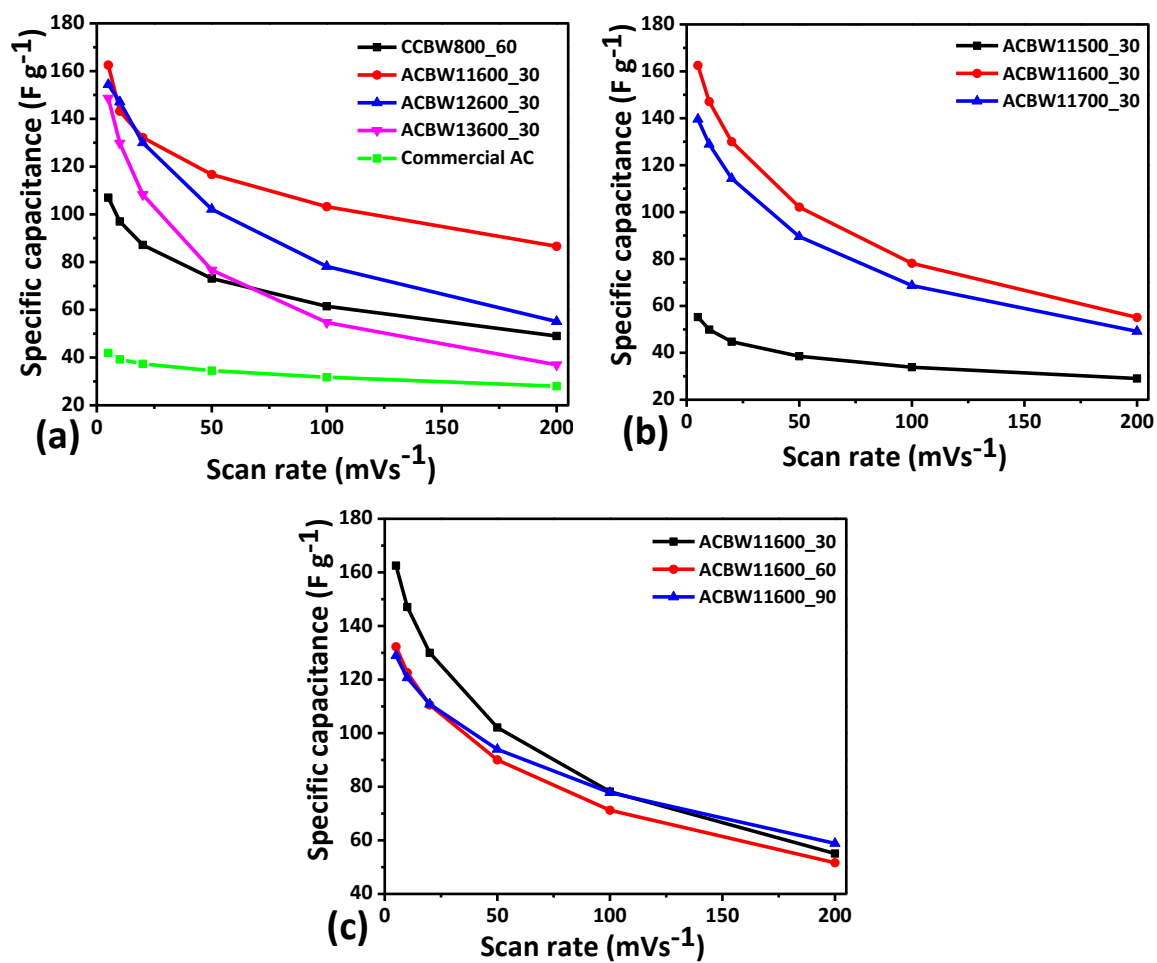


Figure 22: Specific capacitance of commercial AC and ACBW samples at various scan rates as determined from CV by varying (a) activation KOH ratio and (b) temperature, and (c) time in a three-electrode.

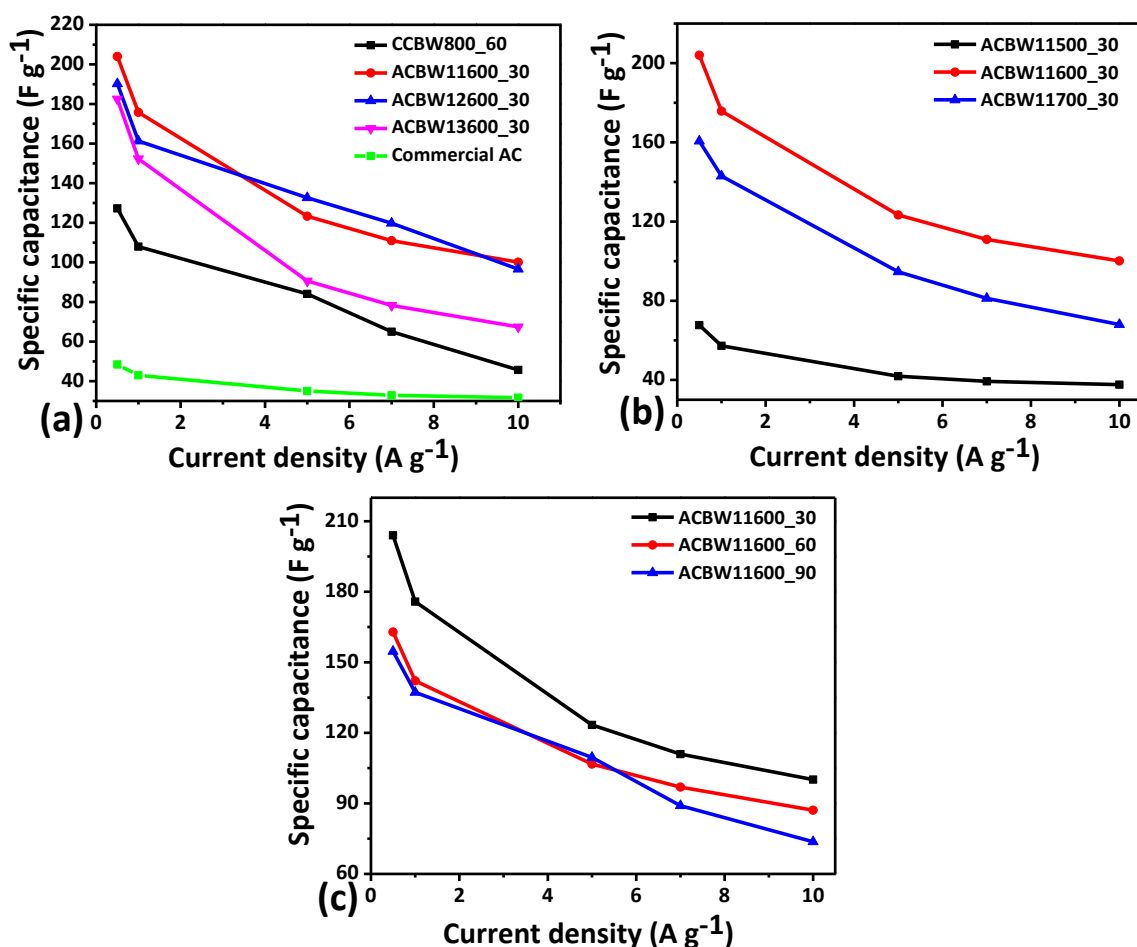


Figure 23: Specific capacitance of commercial AC and ACBW samples at various current densities determined from CCD by differing (a) activation KOH ratio (b), temperature, and (c) time in a three-electrode system.

4.2.3.3 Specific Capacitances for Activated Carbon@NiCo₂O₄ Composite computed from CV and CCD curves

Figure 23 depicts the specific capacitances of activated carbon@NiCo₂O₄ electrode materials prepared at various hydrothermal conditions, as computed from cyclic voltammograms and CCD. In general, increasing the amount of nitrogen doping content causes an increase in capacitance value. High concentration of nitrogen heteroatoms improves the wettability and electrical conductivity of the electrode materials, which significantly enhances capacitance [175], [176]. However, other parameters such as total pore volume and pore size can have a synergistic effect on capacitance and influence the overall performance of electrode materials. At high scan rates, Figure 23 shows that ion diffusion is limited on the surface of the active material indicating that the electric double-layer capacitance dominates over the pseudocapacitance, hence the low specific capacitances [184]. However, Figures 23a and 24(a),

show that when the urea ratio was increased from 15 to 45 mmol, the specific capacitances decreased. Under optimal hydrothermal conditions (15 mmol urea ratio, 140 °C, 6 h), the faradaic reaction favoured by low scan rates, led to an increase in specific capacitance. Additionally, when N interstitials are introduced into crystal structures, oxygen-containing functional groups, help promote reaction kinetics and pseudocapacitance [185]. It can be seen that increasing hydrothermal temperature from 140 to 180 °C did not have any significant increase in specific capacitances (Figures 23(b) and 24b). On the contrary, specific capacitance decreased significantly when the hydrothermal time was increased from 6 to 24 h, Figures 23(c) and 24(c). Figures 23(d) and 24(d) show that NiCo₂O₄/carbon mass loading when increased from 1 to 3 there was a drastic decrease in specific capacitances. This suggests that too much carbon limits the pseudocapacitive behaviour of the nickel-cobaltite spinel structure. However, according to the CCD graph, all materials, except for 1:0.5 and 1:1, have nearly the same specific capacitances at 0.5 A g⁻¹ current density, Figure 24(d). Thus, adding more carbon was not helpful in terms of improving the electrochemical performance in our study. Figures 24(a)-(d) show a decline in specific capacitance with an increase in current density. This is most likely due to an increase in potential drop and insufficient faradaic electrochemical reactions of the NiCo₂O₄ at higher current densities.

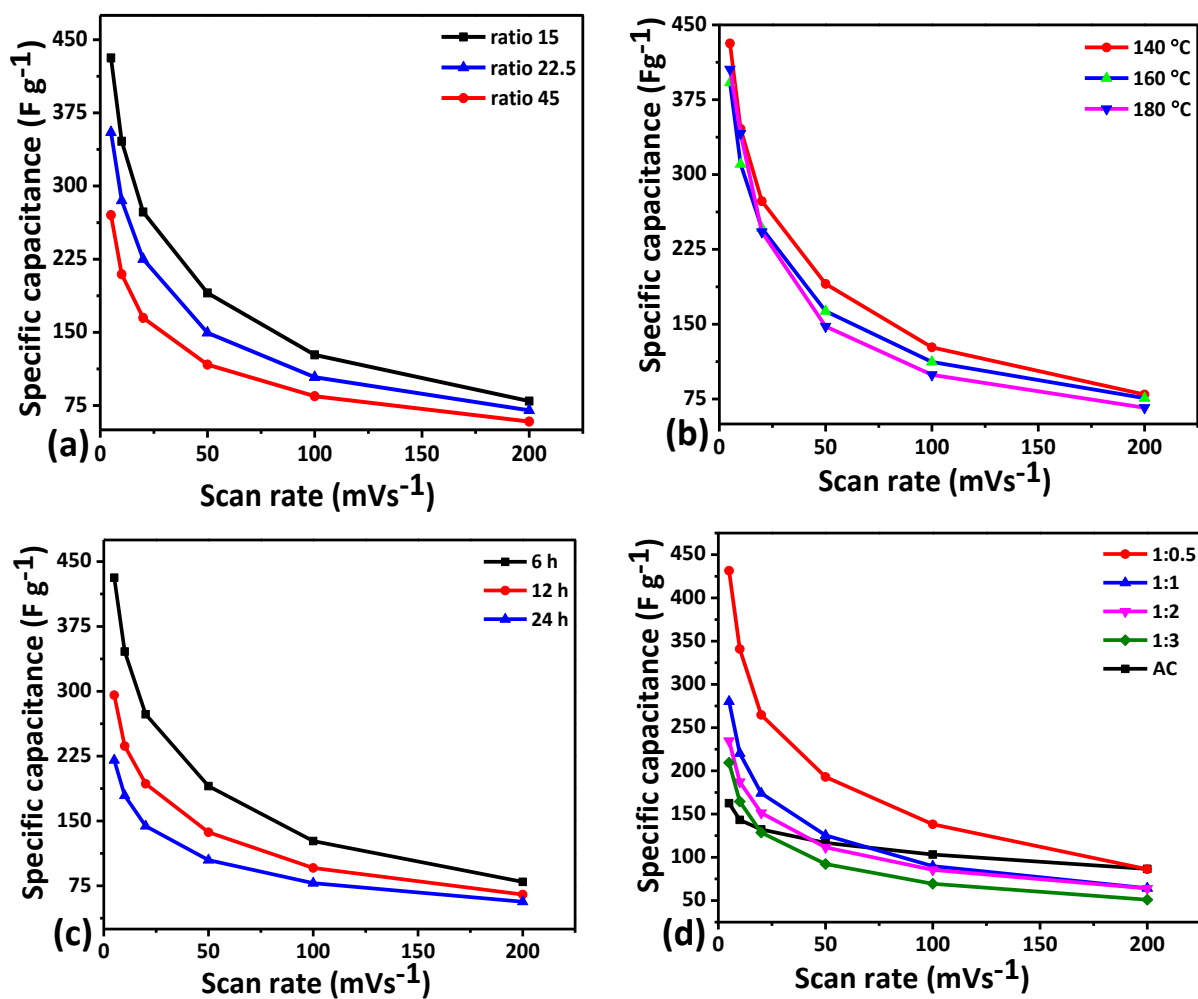


Figure 24: Specific capacitances of AC@NiCo₂O₄ nanocomposites prepared at different hydrothermal urea ratios (a), temperatures (b), times (c), and carbon mass loading (d), at a scan rate of 5 mV s⁻¹

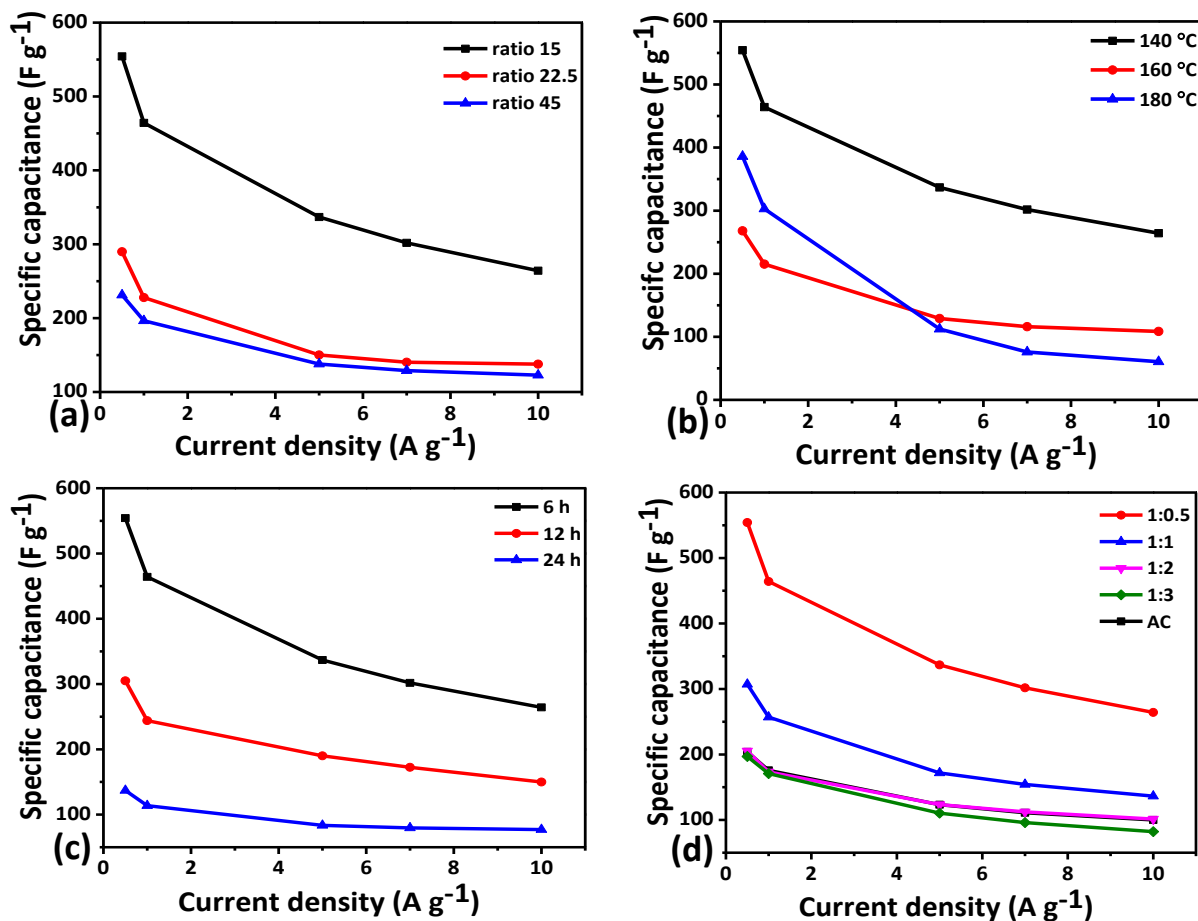


Figure 25: Specific capacitances of AC@NiCo₂O₄ prepared at different hydrothermal urea ratio (a), temperature (b), time (c), and carbon mass loading (d), at different current densities

4.2.4 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is a tool for estimating multifrequency alternating current electrochemically [186]. Over a wide frequency range, it measures the electrical resistance of the electrode/solution interface ranging from 0.01 Hz to 100 kHz. The Nyquist is composed of two parts: a semicircle at the high-frequency zone and a vertical line in the low-frequency zone, demonstrating the capacitance behaviour of the electric double layer (EDL) [187]. At the high-frequency zone, the semi-circle indicates the charge transfer resistance (R_{ct}) of the electrolyte-electrode interface [188], [189], while the Zreal axis intercept of the semi-circle's initial starting point indicates the equivalent series resistance (ESR)/ internal resistance of the electrode material.

4.2.4.1 EIS for Activated Carbon Materials

Figures 25(a)-c and 25(d)-(f) depict the Nyquist and bode plots of ACBW samples, respectively, under various activation conditions. The Nyquist plots show a semicircle in the high-frequency region and an oblique line in the low-frequency region, Figures 25(a)-(c). The

oblique line is attributed to Warburg impedance which is related to the diffusion of electrolytes in the electrode. The internal resistance/ESR can be estimated using the Zreal axis intercept, and charge transport resistance can be determined using the semicircle diameter. The ESR values of all the electrode materials are about 0.22 ohms, revealing high electrical conductivity and rapid ion transit at the solution-electrode boundary. All electrodes prepared in this study demonstrated relatively low charge transfer resistance, in agreement with the negligible diameter of the semicircle depicted in EIS spectra, due to the electrode materials' distinctive porous structure and which enabled rapid electrolyte diffusion [188].

Figures 25(d)-(f) depicts the Bode plots for ACBW electrode materials prepared from different activation conditions, which show the frequency dependence of the phase angle. Observing the phase angle crossing at 45° is used to reveal the electrode materials' ideal capacitive nature [190]. Figure 25d shows that as the activation KOH ratio increased from 1 to 3, the capacitor response frequency increased at a phase angle of -45° . Response frequencies of ACBW electrode materials prepared at different activation temperatures, namely ACBW11500_30, ACBW11600_30, and ACBW11700_30, are 0.08, 0.01, and 0.33 Hz, respectively. The low response frequency suggests that the ACBW11600_30 electrode has a greater surface area for ionic diffusion than the other ACBW electrodes. As the activation time increased from 30 to 90 min, the response frequency at phase angle -45° increases from 0.01 to 0.04 Hz (as shown in Figure 25f). Thus, the ACBW electrode materials prepared from an activation KOH ratio of 1, at 600°C for 30 min showed a rapid frequency response of 0.01 Hz and greater capacitive behaviour than commercial activated carbon, carbonised materials, and other activated carbon materials.

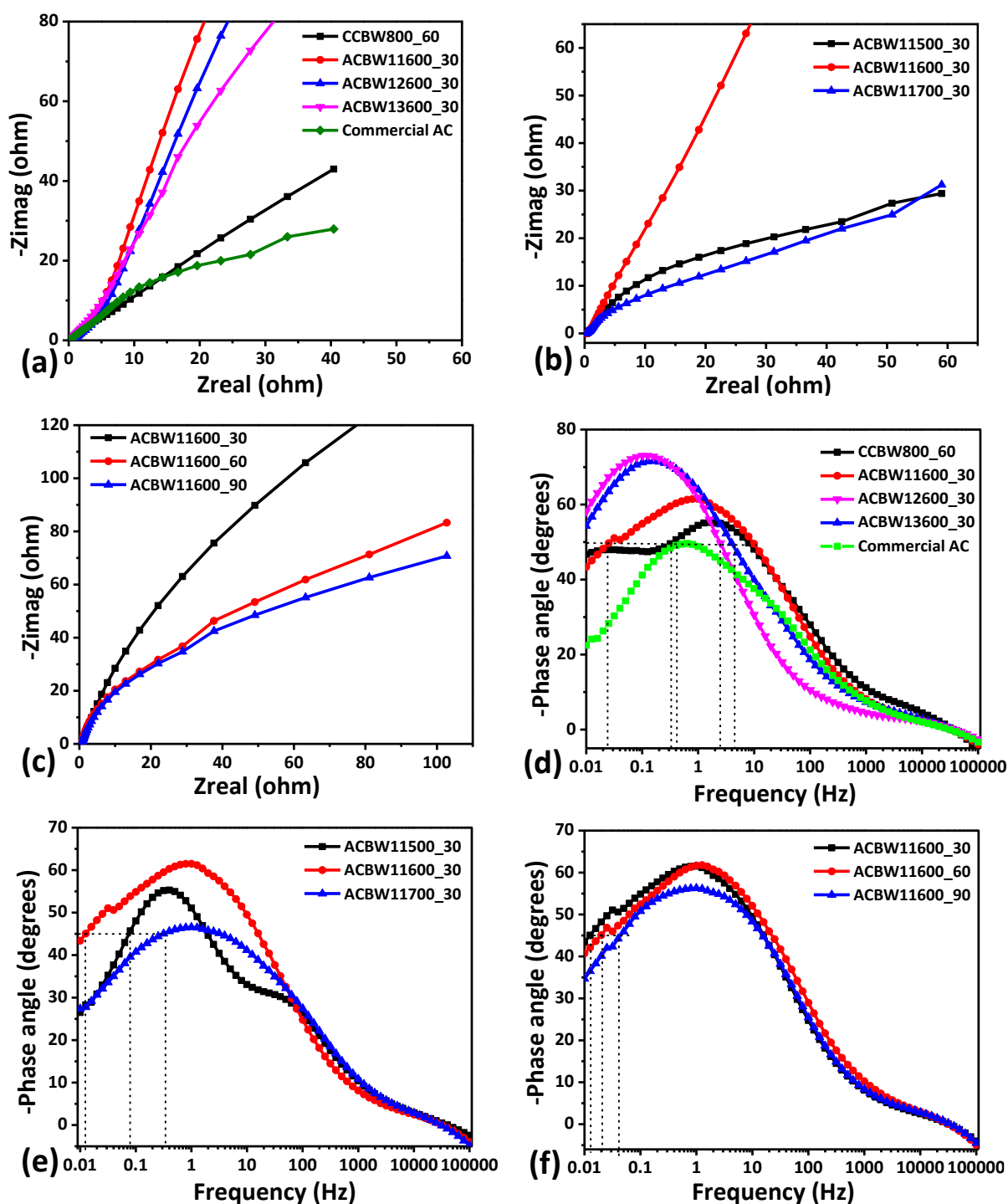


Figure 26: Plots of (a-c) Nyquist and (d-f) bode for ACBW materials prepared from different activation KOH ratios, temperature, and time in three-electrode, in that order.

4.2.4.2 EIS for Activated Carbon@NiCo₂O₄ Composite

The characteristics of activated carbon@NiCo₂O₄ materials were assessed by electrochemical impedance spectroscopy (EIS). Figures 26(a)-(d) show Nyquist plots of activated carbon@NiCo₂O₄ material and Figures 26(e)-(h) show their bode plots in the frequency range of 0.01 Hz-100 kHz. Each impedance spectrum, as shown in Figure 26(a) to (d), contains one

semicircle part in the high-frequency region (see, inset in the lower right of Figures 26a-d) and a trail at low frequencies, which are attributed to charge transfer resistance and Warburg diffusion impedance, respectively [191]. At high frequencies, the shape of the Nyquist plots deviates from the standard semicircle, which is because of the heterogeneous nature of the electrode/solution interface, which slows the faradaic process. [192], [193]. The charge-transfer and equivalent series resistances increase with the increase in urea ratio, temperature, and carbon mass loading, Appendix E. Activated carbon@NiCo₂O₄ material hydrothermally treated at 140 °C for 6 h (N-doped with N at 5 mmol), exhibited the smallest ESR of 0.35 ohms and charge-transfer resistance of 0.52 ohms compared to other materials, showing that the material has higher performance than others.

Figure 26(e)-(h) depicts a phase angle vs frequency plot used to investigate the capacitive nature of electrode materials. A phase angle greater than 45° favours the electrode's capacitive performance, while a phase angle less than 45° reflects the electrode's resistive behaviour [112]. Activated carbon@NiCo₂O₄ electrode materials have a phase angle greater than 45° in the low-frequency region, indicating capacitive behaviour. Hydrothermal conditions, on the other hand, were found to influence the phase angle. When the urea ratio was increased from 15 to 22.5 mmol, the phase angle dropped significantly from -55 to -49°, then increased to 53° when the ratio was increased to 45 mmol, as shown in Figure 26(e). Similarly, as the hydrothermal temperature increased from 140 to 160 °C, the phase angle decreased from -55 to 49° (Figure 26f). At a high hydrothermal temperature of 180 °C, the phase angle is -60°, which is close to the -90° phase angle of an ideal capacitor. Figure 26(g) shows that as hydrothermal time increased, the phase angle decreased. When the carbon mass loading was increased from 1 to 3, the phase angle shifted slightly (Figure 26h). The bare activated carbon produced from cattle blood waste had a phase angle of less than 45° when compared to all Activated carbon@NiCo₂O₄ materials synthesized in our study, indicating the resistive nature of the carbon material. Thus, combining activated carbon with NiCo₂O₄ improved carbon materials' capacitive behavior and specific capacitance of the carbon materials.

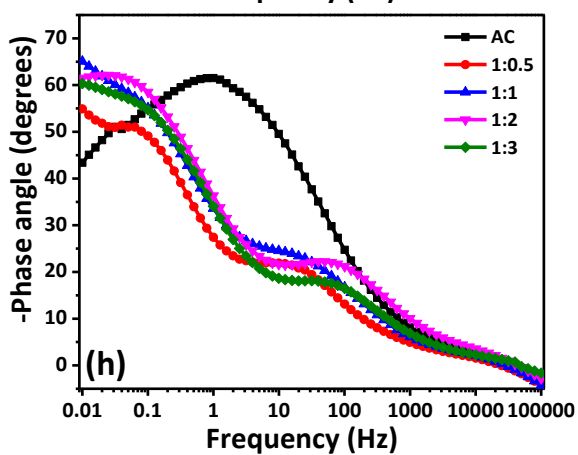
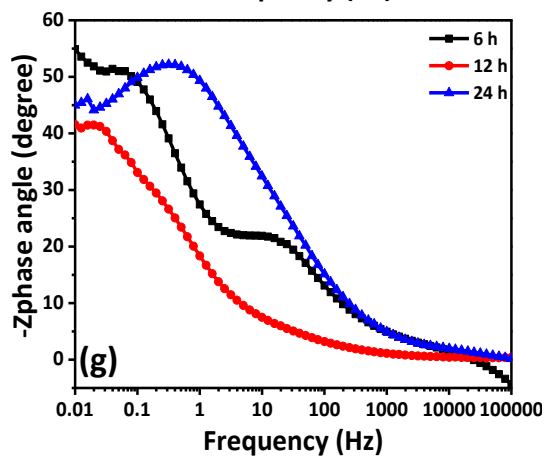
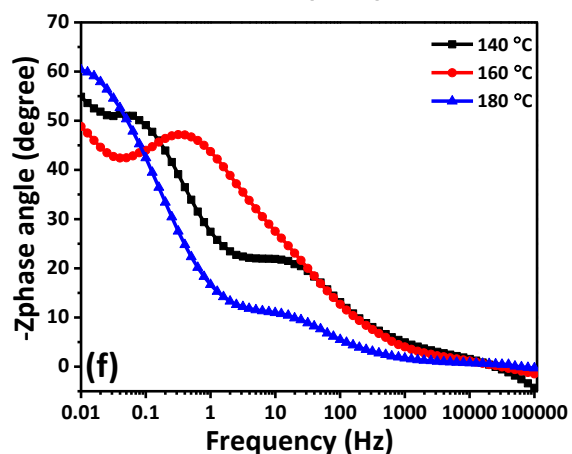
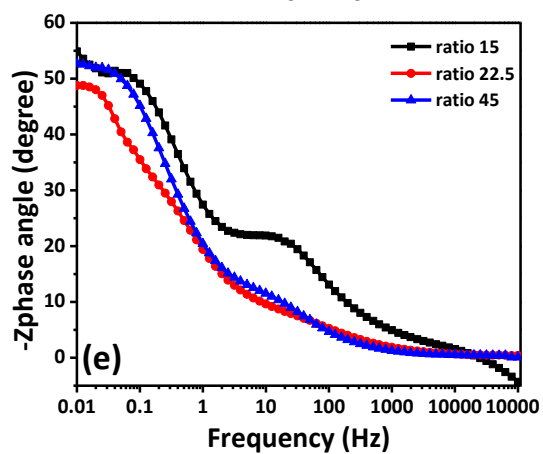
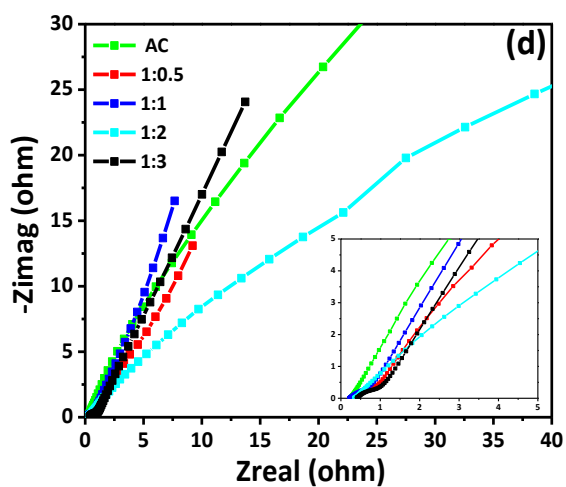
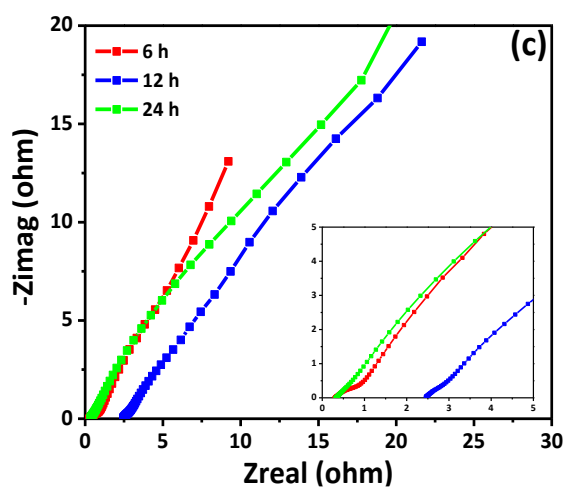
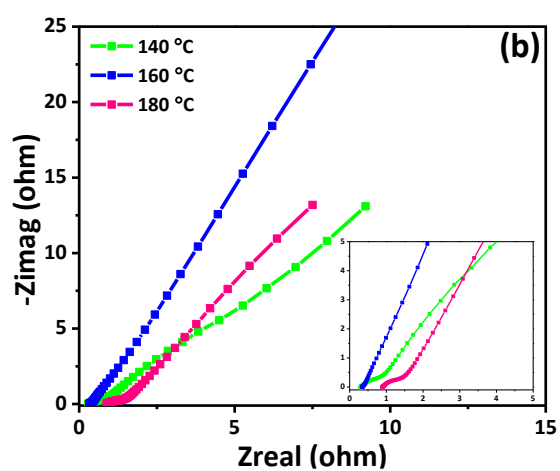
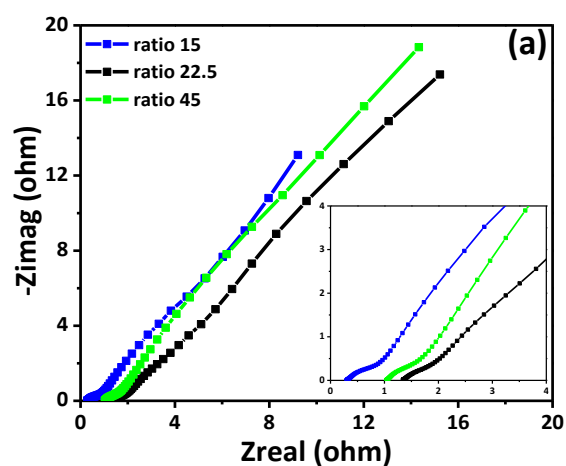


Figure 27: (a–d) Nyquist and (e–h) bode plots for Activated carbon@NiCo₂O₄ samples at different (a and e) hydrothermal urea ratios, (b and f) temperature, (c and g) time, and (d and h) carbon mass loadings in three-electrode.

4.2.5 Cyclic Stability Studies

Another critical factor for supercapacitors is cycling stability [194]. The cyclic stability of supercapacitors is determined by the electrode materials, which are the core components. At 10 A g⁻¹, continuous CCD measurements were taken over a period of 5000 cycles. Figure 27 depicts capacity retention and coulombic efficiency. ACBW11600_30 retained 75% of its initial capacitance after 5,000 cycles at 10 A g⁻¹, indicating outstanding structural and cycle stability. The porous structure, which aids ion diffusion during charge/discharge, could be attributable to higher cycle stability. Additionally, the electrode material has a high coulombic efficiency of 103% indicating good reversibility during cycling. However, it is observed that with the incorporation of nickel-cobaltite the electrodes' capacitance retention and coulombic efficiency increased to 100 and 100%, respectively, indicating that NiCo₂O₄ facilitates an improvement in electron transfer, which helps to amplify the specific capacitance and the reversibility of the charge transfer of the composite materials [78].

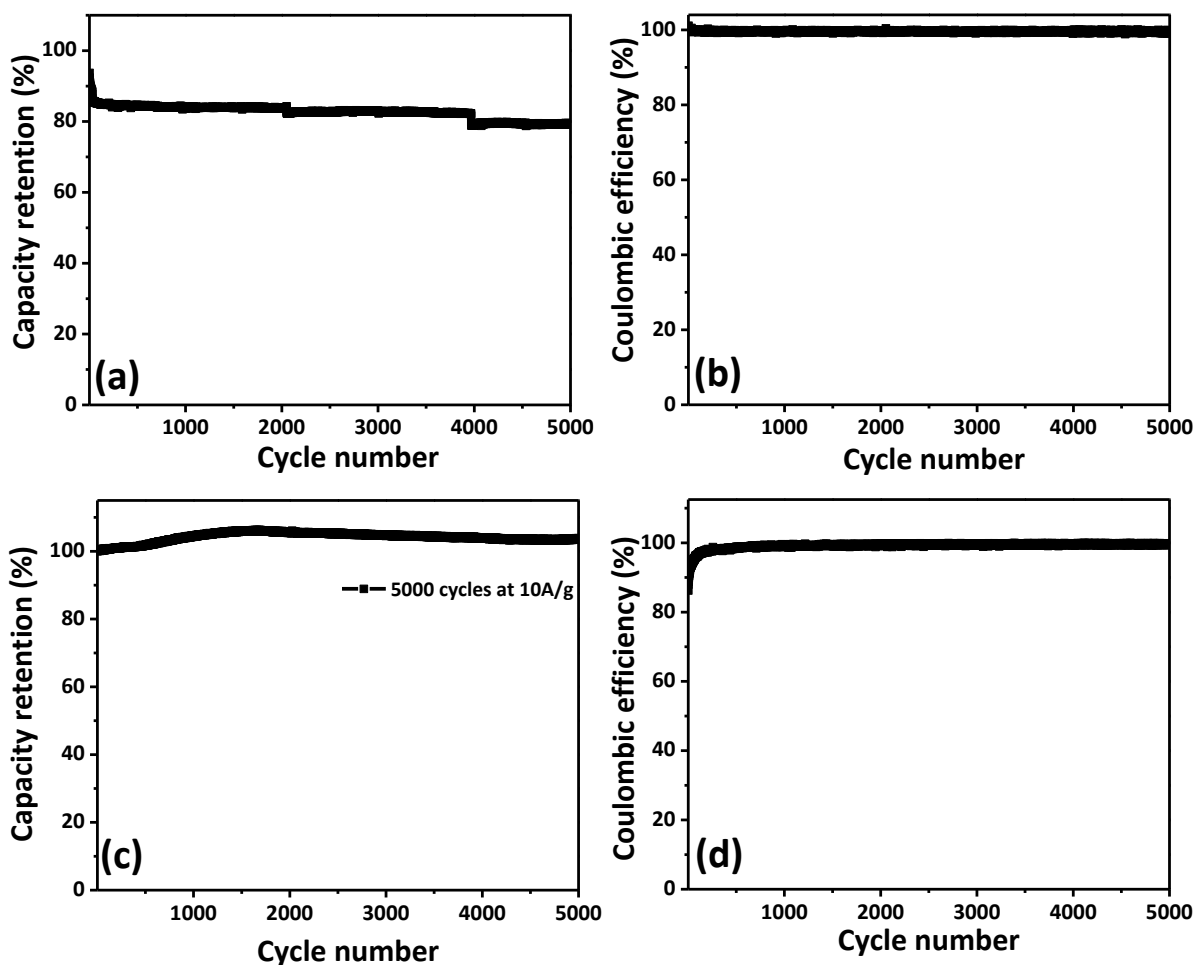


Figure 28: Capacity retention and coulombic efficiency over 5000 cycles of (a-b) ACBW11600_30, and (c-d) activated carbon@NiCo₂O₄ at a current density of 10 A g⁻¹ in three-electrode

4.3 Electrochemical Test- Two Electrode System for As-synthesised Carbon & Activated Carbon Materials

Furthermore, carbon-based electrode materials prepared were tested for real-world symmetric device application in a two-electrode configuration. The cyclic voltammetry and cyclic charge-discharge measurements were taken in the 0.0 to 1.0 V voltage range to evaluate the electrochemical performance of activated carbon electrode materials.

4.3.1 Cyclic Voltammetry

To investigate the practical applications of ACBW samples, we built symmetric supercapacitor devices and tested their properties in 6 M KOH (Figure 28). The cyclic voltammograms had a slightly distorted rectangular-like shape at 200 mV s⁻¹ sweep rate, attesting to the as-

synthesized carbon materials' good EDL capacitive behaviour and the ACBW electrodes' good electrochemical reversibility. When comparing the non-activated samples and other ACBW samples activated in different conditions, the ACBW11600_30 electrode had the highest current response and largest area under the cyclic voltammograms. The electrodes' high surface area and structural defects contributed to their great capacitive behavior (Figure 28b-d).

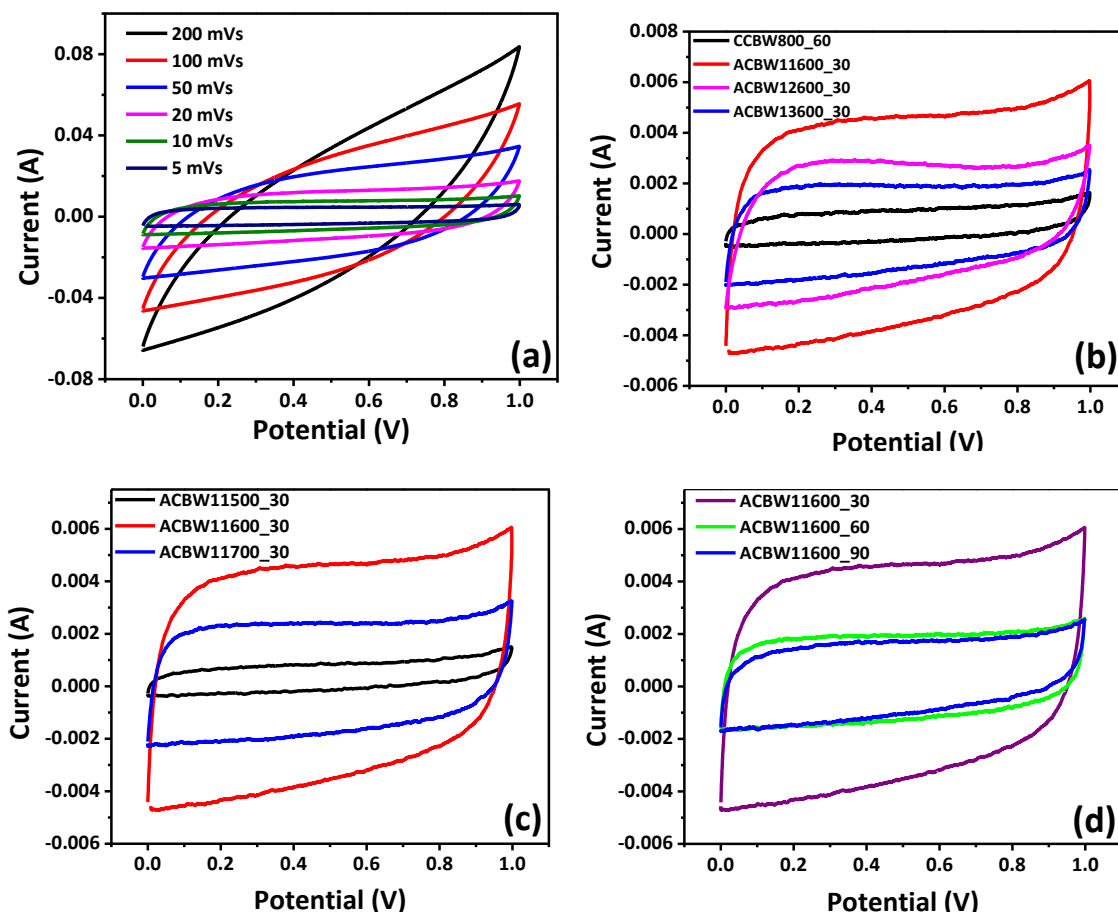


Figure 29: Cyclic voltammograms of (a) ACBW11600_30 material at different scan rates of 5-200 mV s^{-1} and (b-d) ACBW electrode materials prepared at different activation ratios, temperatures, and times in a two-electrode setup, in that order.

4.3.2 Cyclic Charge-Discharge

The cyclic charge-discharge curves of the ACBW11600_30 electrode at current densities that range from 0.2 to 1 A g^{-1} are shown in Figure 29(a), whereas Figures 29(b) to (d) depict electrodes prepared from various ACBW materials at different activation KOH ratios, temperatures, and times at 0.2 A g^{-1} current density. All the CCD curves have a normal triangular shape and a small IR drop, indicating great charge-discharge reversibility, and electrodes that have low internal resistance. The discharge time decreased when activation

temperature increased from 600 to 700 °C, Figure 29(c). Similarly, as activation time increased from 30 to 90 min, the discharge time decreased (Figure 29d). This implies that at high activation temperatures and long activation times, the microstructure of carbon materials is destroyed, limiting the active sites for charge adsorption, and lowering specific capacitance [195]. It is also noteworthy that the discharge time for ACBW11600_30 electrode material is longer than that of ACBW12600_30 and ACBW13600_30 electrodes, implying that capacitance improved as the activation KOH ratio decreased. All ACBW carbon-based electrodes had a prolonged discharge time than the commercial activated carbon, highlighting the exceptional electrochemical behaviour of the carbon-based electrode materials developed in our research work (Figure 29e).

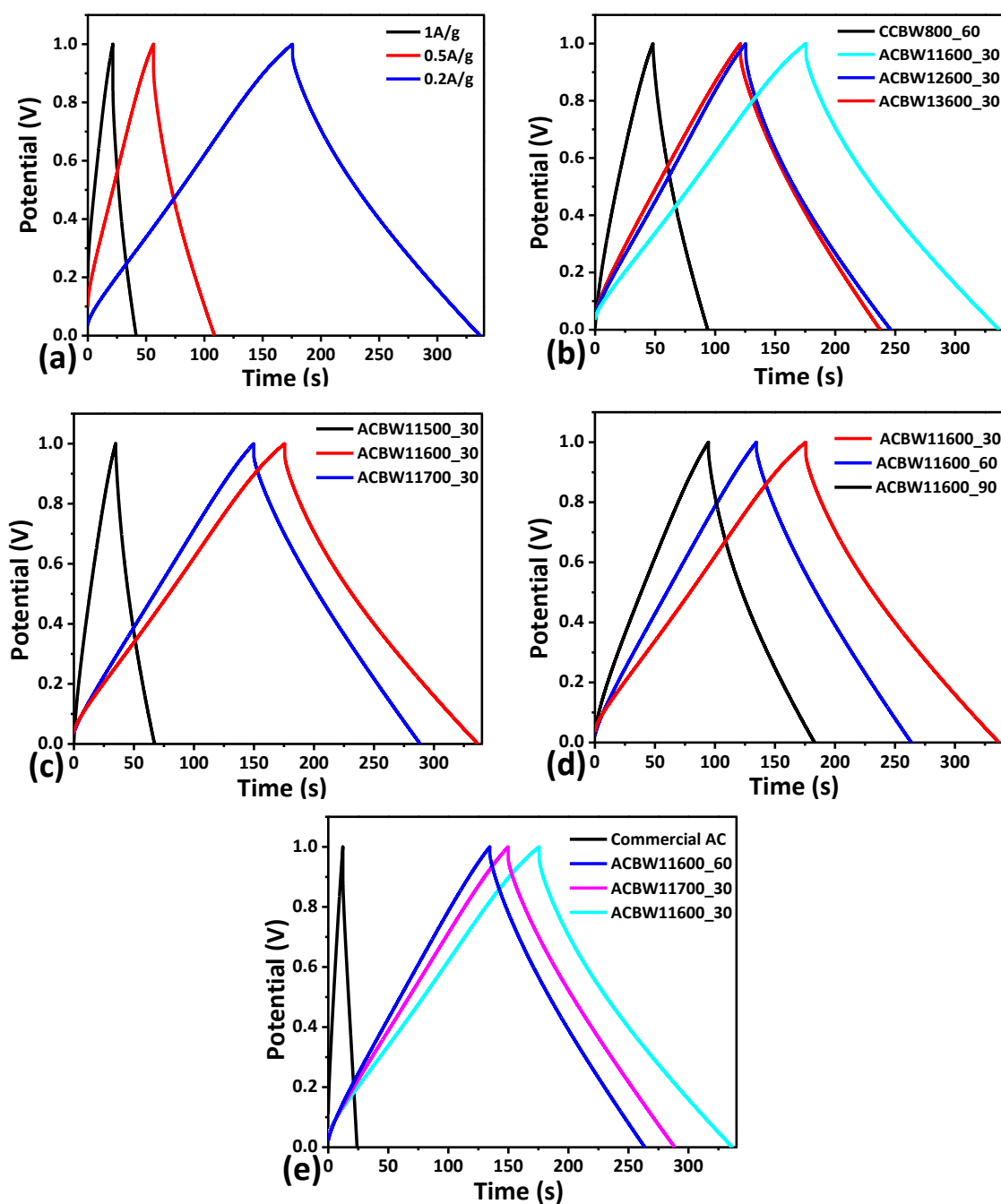


Figure 30: Cyclic charging - discharging curves of (a) ACBW11600_30 electrode at different current densities, (b)-(d) electrodes prepared from ACBW samples at various activation KOH ratios, temperature, and time and (e) ACBW samples compared to discharge time for commercial AC at 0.2 A g^{-1} in two-electrode experiments.

4.3.3 Specific Capacitance from CV and CCD

Figures 30 and 31 show specific capacitances of ACBW electrodes tested in symmetric supercapacitor devices at various scan rates and current densities. As is well known, at

low scan rate and current density, the electrolyte has enough direct interaction with the electrode layer, resulting in high specific capacitances.

Figures 30 (a)-(c) and 31 (a)-(c) demonstrate that decreasing the activation KOH ratio increased specific capacitances, whereas increasing activation time and temperature did not result in any significant improvement in electrochemical performance. Materials carbonised at 800 °C and activated at KOH ratio 1:1 at 600 °C for 30 min afforded 119.6 and 144.7 F g⁻¹ specific capacitances at 5 mV s⁻¹ and 0.2 A g⁻¹, respectively. The high BET-specific surface area provided an adequate number of active sites for the electrolyte ions, resulting in this impressive performance. All electrodes prepared from ACBW samples showed excellent capacitive behaviour, characterized by high specific capacitance compared to commercial activated carbon, which makes our ACBW materials to be superior and suitable for real device supercapacitor applications.

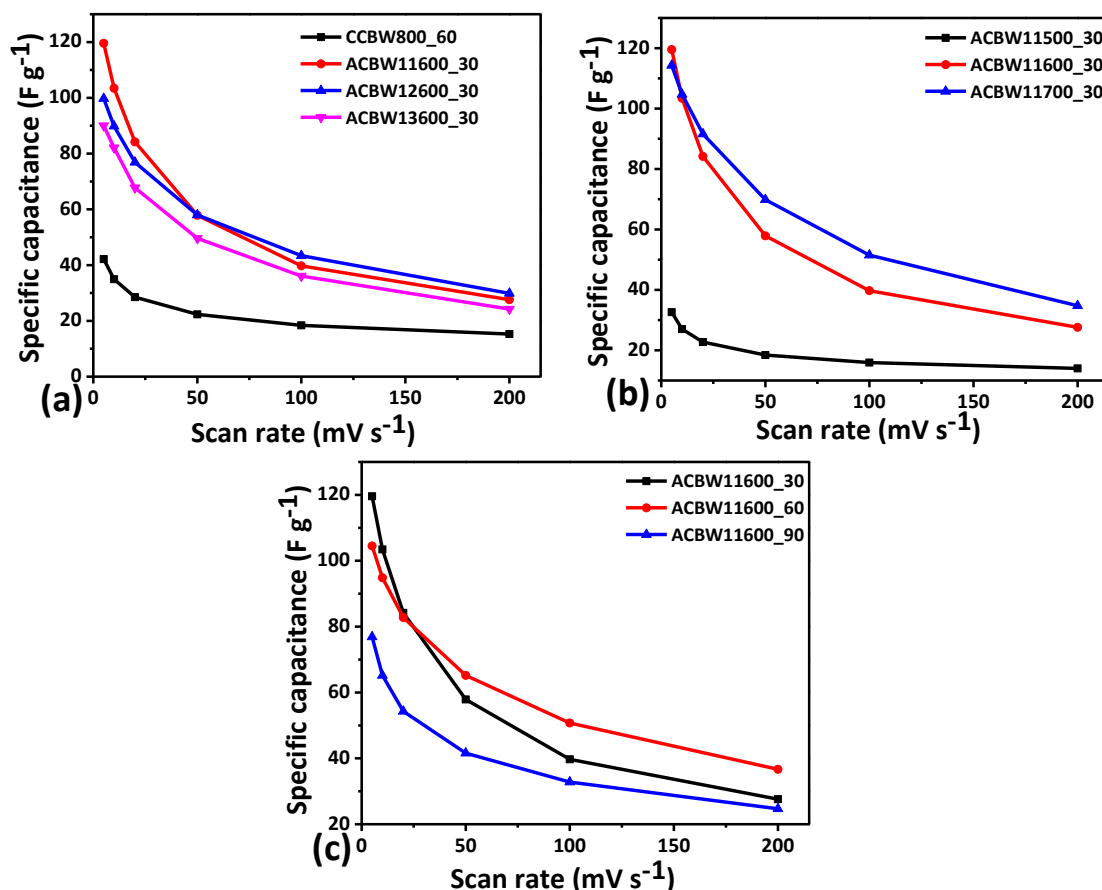


Figure 31: Specific capacitance of commercial AC and ACBW samples in a two-cell system at various scan rates and activation conditions (a) activation KOH/carbon ratio, (b) temperature, and (c) time, computed from CV.

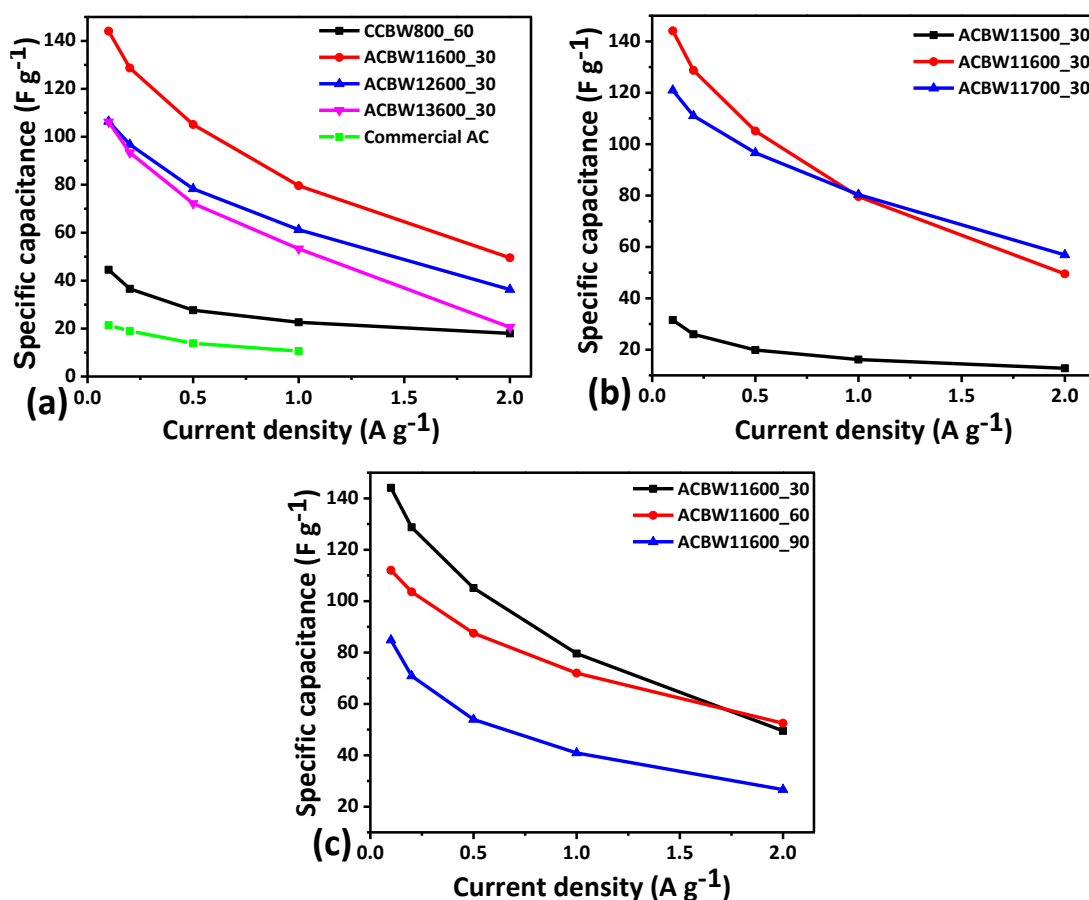


Figure 32: Specific capacitance of commercial AC and ACBW samples at various current densities and activation conditions (a) activation KOH ratio, (b) temperature, and (c) time in a two-electrode system, computed from CCD data.

4.3.4 Electrochemical Impedance Test

Figure 32 depicts the EIS spectra for all electrode materials, measuring their impedance over a range of frequencies from 0.01 Hz-100 kHz. The intercepts of the Zreal axis and the diameter of the semicircle in high frequency correspond to equivalent series resistance (ESR) and charge transfer resistance (R_{ct}), respectively. The ESR of all samples is 0.20 ohm, indicating a quicker charge transition and good electrical conductivity. As the activation KOH ratio increased from 1 to 3 (Figure 32a), the activation temperature increased from 600 to 700 °C (Figure 32b), and the time increased from 30 to 90 min, the R_{ct} increased (Figure 32c). ACBW11600_30 has the smallest R_{ct} . ESR has also been found to cause the accumulation of dissipated energy. High ESR and IR drop values can significantly reduce energy and power efficiency due

to charge flow resistance. Therefore, low resistance in a system improves electrolyte ion diffusion rate and results in higher power density [196].

The relationship between frequency and phase angle is shown in Figure 32 (d-f). The phase angle dropped significantly from -71 to -56° at low frequency when the activation KOH ratio was gradually increased to 3 as shown in Figure 32d. ACBW11600_30 has a phase angle of -69° , which is very close to the -90° phase angle of an ideal capacitor. This explains why these materials have such good capacitive behaviour (high specific capacitance). Similarly, there was no substantial change in phase angle as activation temperature increases from 500 to 700°C , as shown in Figure 32e. In Figure 30(f), a slight shift in phase angle occurred as activation time increased from 30 to 90 min.

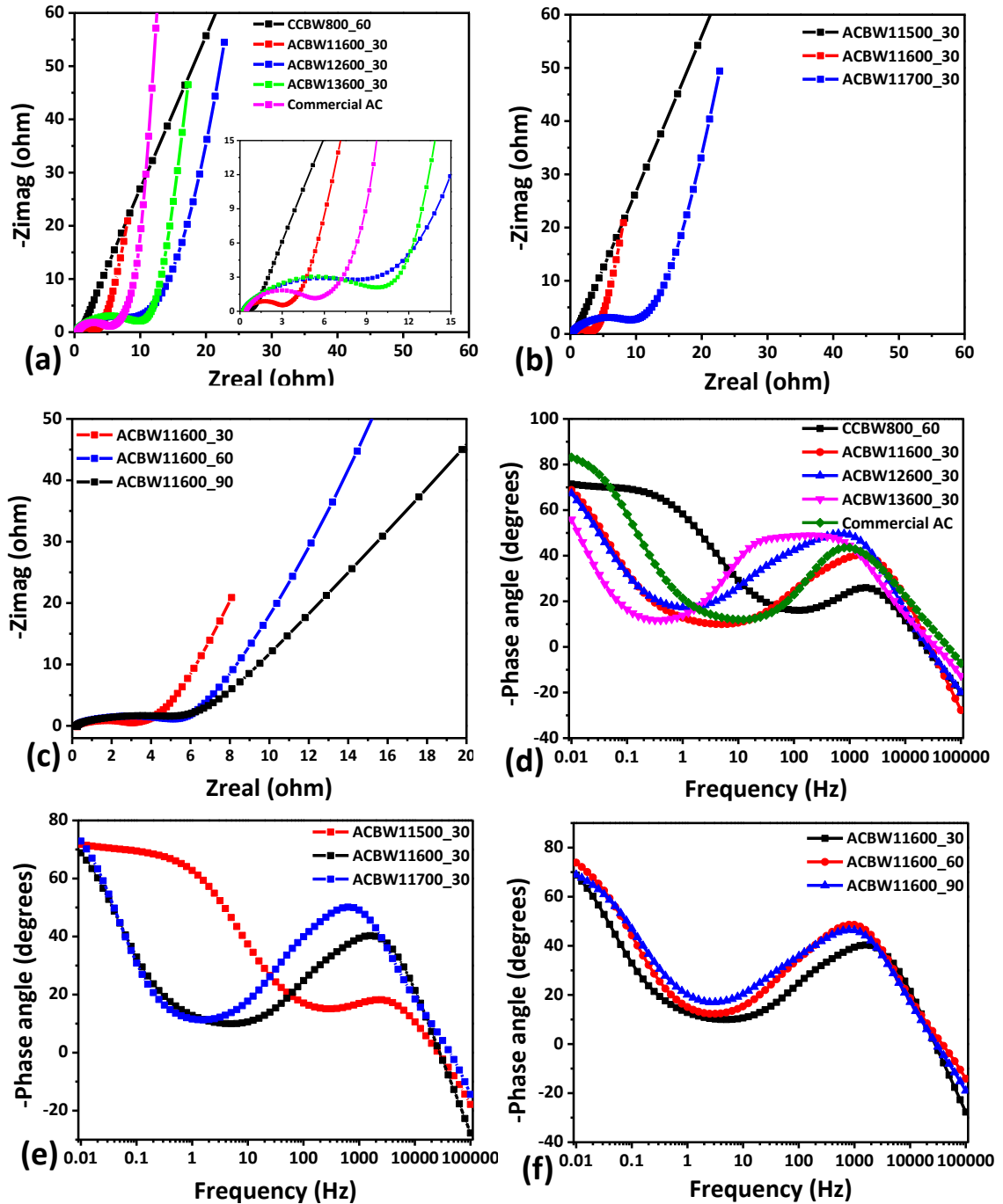


Figure 33: Plots of Nyquist (a-c) and bode (d-f) of ACBW electrode materials in a two-cell system at various activation KOH ratios, temperature, and time, in that order.

4.3.5 Stability and Ragone plot

The cycle stability of materials is a critical consideration in determining their suitability for practical supercapacitor applications. Figure 33(a) and (b) depicts the cycling performance and coulombic efficiency of the ACBW11600_30 and ACBW11700_30 electrodes in a two-electrode system when tested at 2 A g^{-1} . After 5,000 charge-discharge

cycles, the electrodes ACBW11700_30 and ACBW11600_30 retained 89 and 91% of their initial capacitance, respectively, with 100% coulombic efficiency, indicating the electrodes' outstanding cycling stability and good rate capability [197].

EIS measurements were also performed on the ACBW11700_30 and ACBW11600_30 electrodes after 5000 cycles at 2 A g^{-1} , as shown in Figures 33(c) and (d), respectively. At extremely low frequencies, the intercept of the Zreal axis represents the sum of the electrolyte's ionic resistance, the active materials resistance, and the contact resistance between the active material-current collector interface [198], [199]. Even after 5000 cycles, the electrodes ESR remained remarkably low. Furthermore, the distance of the semicircle expanded over 5000 charge-discharge cyclings, indicating an increase in R_{ct} thus extending electron transport pathways [200]. ACBW11600_30 charge-transfer resistance increased from 4 (pre-cycle) to 11 ohms (post-cycle), while that of the ACBW11700_30 increased from 10 (pre-cycle) to 15 ohms (post-cycle), Figure 33 c-d.

The Ragone plots for electrodes prepared from ACBW samples in the two-electrode configuration are shown in Figure 33(e). When compared to other ACBW samples and commercial AC, the ACBW11600_30 symmetric supercapacitor device achieved an excellent 20.1 Wh kg^{-1} energy density at 200 W kg^{-1} power density and maintained 6.9 Wh kg^{-1} at 4000 W kg^{-1} . The ACBW carbon-based electrodes prepared in this study show outstanding electrochemical performance compared to those reported in the literature (Table 5). The presence of micropores provided charge accommodation and fast ions transport channel and oxygen functional groups provided additional pseudocapacitance, implying that the electrodes could be utilised in fast-charging devices.

Table 4: Electrochemical performance of carbon-based electrodes from previous works compared to present work

Carbon derivation	Activation route	S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	Electrolyte	C_{sp} (Fg^{-1}) 2-Electrode	E (Wh kg^{-1})	CR (%)	Ref
N-doped pomelo mesocarps based nanosheet	CaCl_2	974.6	0.5 M Na_2SO_4	112 at 0.25 A g^{-1}	14	96.5 at 1 A g^{-1} (10000 cycles)	[201], [202]
Fibers of palm oil empty fruit bunches	$\text{KOH} + \text{CO}_2$	1704	1 M H_2SO_4	149	4.3	-	[202]
Agricultural waste cornhusk	KOH	1109	seawater	130 at 0.5 A g^{-1}	7.4	95 (1000 cycles)	[203]
Milk-free coconut kernel pulp	KOH	1200	1 M TEABF_4 in PC	56 at 0.25 A g^{-1}	-	100 at 2 A g^{-1} (2000 cycles)	[204]
Cattle blood waste	KOH	321	6 M KOH	144 at 0.2 A g^{-1}	20	91 at 2 A g^{-1} (5000 cycles)	This work

S_{BET} = BET specific surface area, C_{sp} = Specific capacitance, E= Energy density, CR%= Capacity retention.

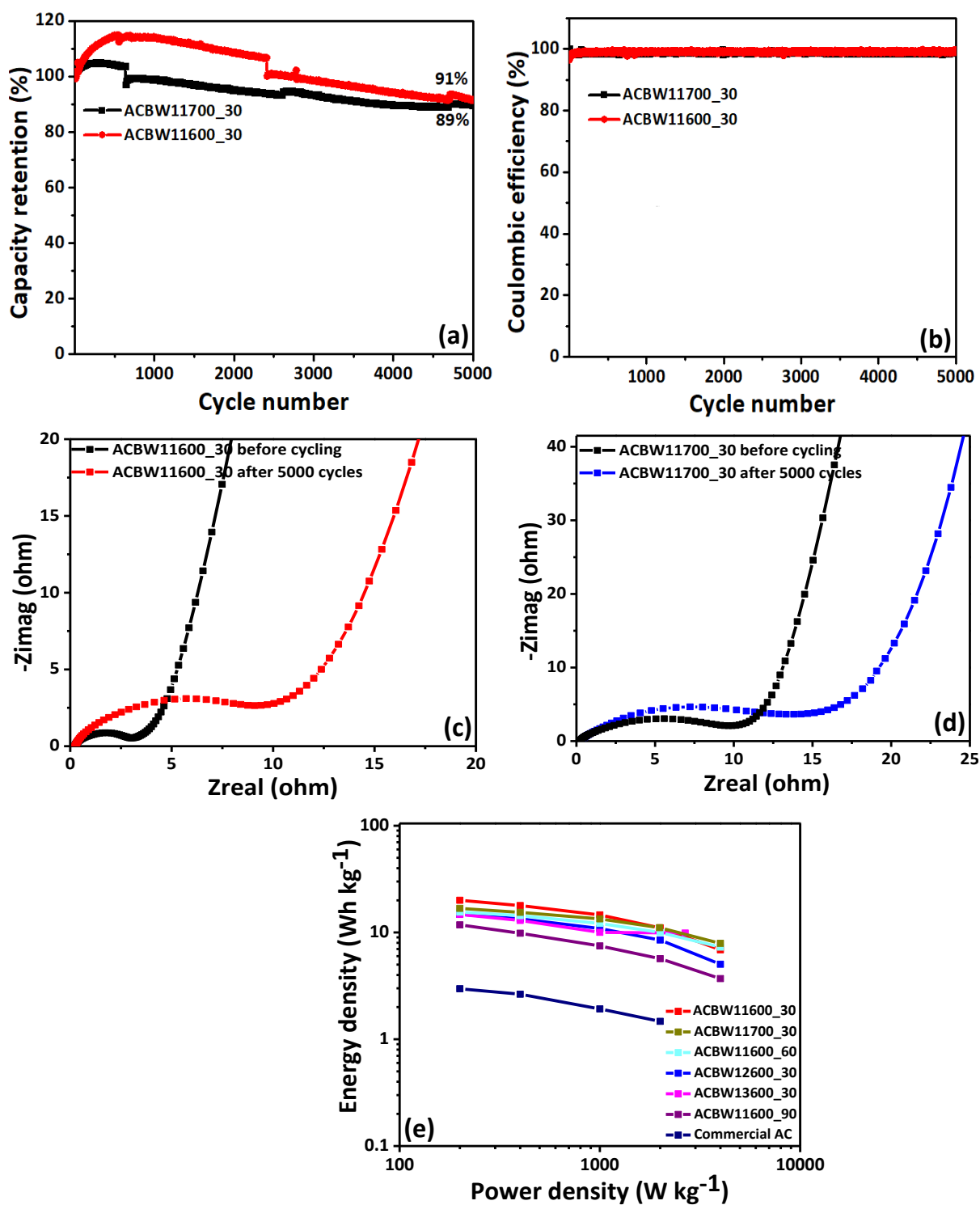


Figure 34: Capacity retention (a) and coulombic efficiency (b) recorded for 5000 cycles at 0.2 A g⁻¹. Nyquist plots (c-d) for ACBW11600_30 and ACBW11700_30 before and after cycling and (e) Ragone plot depicting power and energy density of as-prepared electrode materials.

5 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Low-cost, as well as abundant activated carbon electrode materials derived from cattle blood waste, were successfully synthesized through carbonisation followed by KOH and chemical activation. The physicochemical properties of the prepared materials were characterized using an X-ray diffractometer (XRD), Fourier transform infrared (FTIR), Scanning electron microscopy (SEM), Raman spectroscopy, Thermal gravimetric analysis (TGA), Brunauer-Emmett-Teller (BET) and Transmission Electron Microscopy (TEM) techniques. The materials were tested for their electrochemical performance using both three and two-electrode configurations and 6 M KOH as electrolyte. The electrochemical tests revealed that the specific capacitance was influenced by carbonisation temperatures, and activation conditions (KOH ratio, time, and temperature). As the KOH activation ratio increased from 1 to 3, charge transfer resistances decreased, and the phase angle decreased from -71 to -56° at low frequency. ACBW11600_30 had the highest specific capacitances of 164 and 204 F g^{-1} in a three-electrode system at a scanning rate of 5 mV s^{-1} and a current density of 0.5 A g^{-1} . The ACBW11600_30 symmetric supercapacitor device achieved specific capacitance of 119.3 and 144.90 F g^{-1} from cyclic voltammetry and cyclic charge-discharge measurements, respectively, at a scan rate of 5 mV s^{-1} and a current density of 0.1 A g^{-1} . After 5000 charge-discharge cycles, the device retains capacity at 91 and 100% coulombic efficiency. Furthermore, activated carbon@NiCo₂O₄ was successfully synthesised via the hydrothermal treatment method. The as-synthesized activated carbon@NiCo₂O₄ materials were characterized using XRD, SEM, TEM, FTIR BET, and Raman spectroscopy techniques. The materials were tested for their electrochemical performance using a three-electrode configuration and 6 M KOH as electrolyte. The study found that incorporating NiCo₂O₄ into carbonaceous material increased the specific capacitance. ACBW11600_30 symmetric real device achieved approximate energy densities of 20 W h kg^{-1} and power density of 200 W kg^{-1} . Therefore, carbon materials derived from cattle blood waste have enormous potential for use in supercapacitor device applications, according to this study.

5.2 Recommendations for Future Work

- i. A stability test for activated carbon symmetric real device for supercapacitors at 20000 cycles at higher current density should be carried out.
- ii. Perform additional characterization, such as XPS and elemental analysis, to determine the surface composition of heteroatoms (e.g N, O, Fe, C, and S) in the materials and how it affects electrochemical activity.
- iii. A two-electrode system electrochemical testing for activated carbon@NiCo₂O₄ composite in asymmetric hybrid supercapacitor device and determine energy density and power density.

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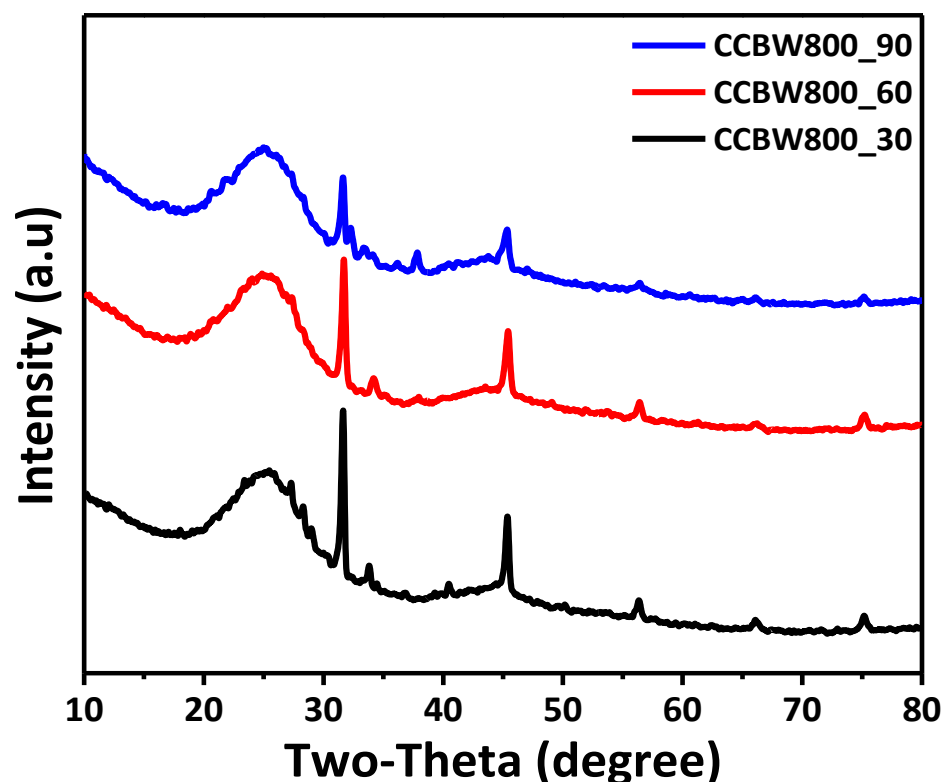
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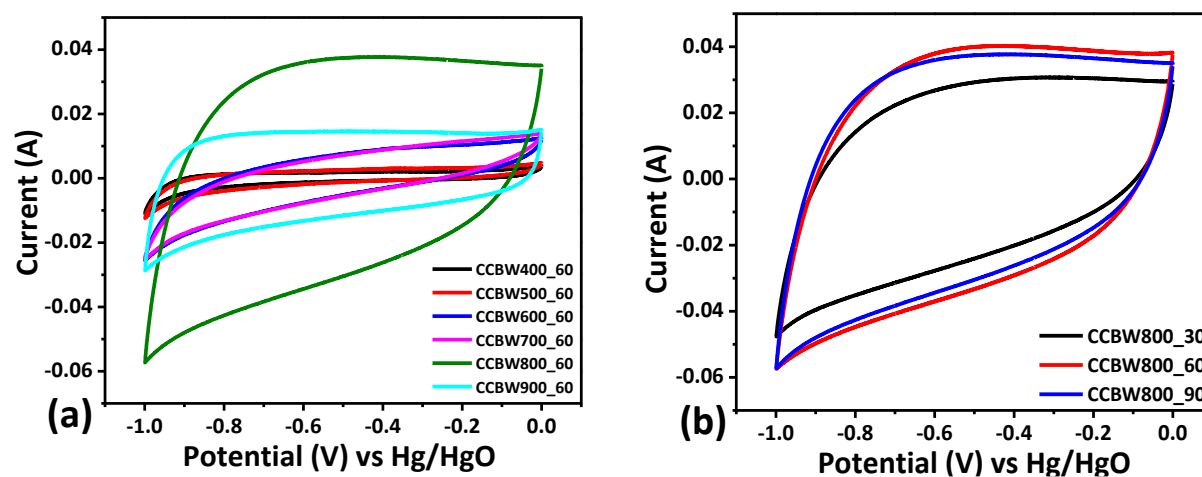
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APPENDIX

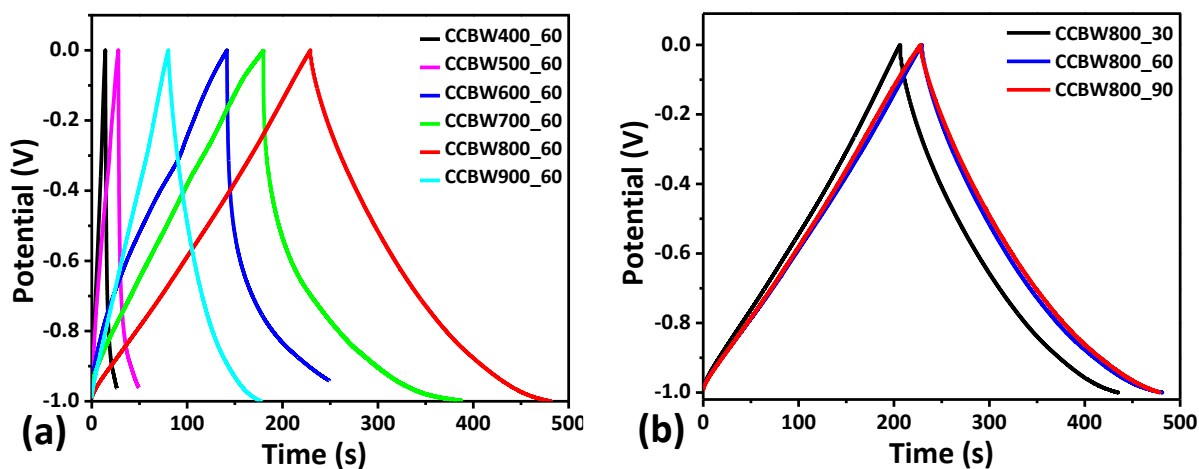
Appendix A: XRD patterns for CBW materials at different carbonisation temperature and time



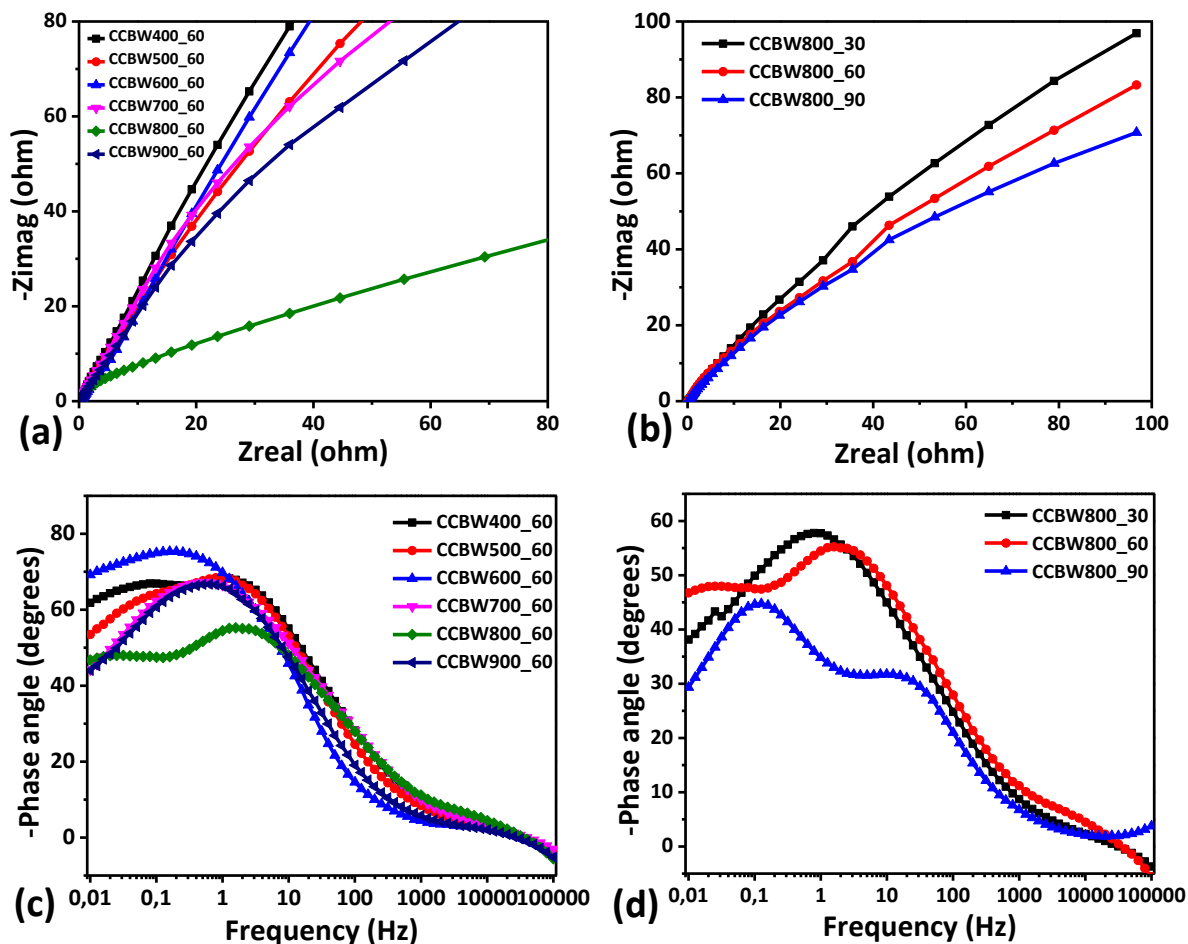
Appendix B: Cyclic voltammograms of CCBW materials at different carbonisation temperatures and time at scan rate of 100 mVs^{-1}



Appendix C: Cyclic charge discharge curves of CCBW materials at different carbonization temperature and time at current density of 0.5 A g^{-1}



Appendix D: Nyquist and bode plots for CCBW materials



Appendix E: EIS characteristics of NiCo₂O₄/AC electrode materials

Hydrothermal condition	ESR (ohm)	Charge-transfer resistance (ohm)
Urea ratio (mmol)		
45	1.38	0.62
22.5	1.08	0.57
15	0.35	0.52
Temperature (°C)		
180	0.91	0.57
160	0.36	-
140	0.35	0.52
Time (hrs)		
24	0.36	-
12	2.25	0.55
6	0.35	0.52
Carbon mass loading (w/w%)		
1:3	0.44	0.56
1:2	0.37	-
1:1	0.24	0.57
1:0.5	0.35	0.52