

**SYNERGIZING OPTIMIZED ELECTRODE
ELECTROLYTE INTERFACE FOR HIGH ENERGY
DENSITY SUPERCAPACITORS APPLICATION**

BY

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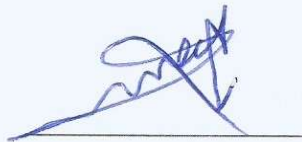
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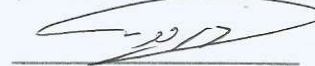
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DEDICATION

This piece of work is dedicated to Almighty Allah who has given me the strength and ability to complete this project and to my beloved parents, Alh. Dahiru Shuaibu and Haj.

Sadiya Umar for their unrelenting support, guidance, and prayers, may Allah (S.W.T) grant them the highest rank in Jannah, Amin.

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LIST OF ABBREVIATIONS

ARS:	Alizarine
AQ:	Anthraquinone
AQQS:	Anthraquinone Sodium
BJH:	Barrett-Joyner-Halenda
BET:	Brauna Emmet Teller
BQ:	Benzoquinone
CPEs:	Composite Polymer Electrolytes
CV:	Cyclic Voltammetry
DSAC:	Date Stone Activated Carbon
DSDC:	Date Stone-derived Cellulose
DMC:	Dimethyl Carboxylate
DMF:	Dimethyl Formamide
DSC:	Differential Scanning Calorimetry
DMSO:	Dimethyl Sulfoxide
EDLC:	Electrochemical Double Layer Capacitor
EIS:	Electrochemical Impedence Spectroscopy
EC:	Ethylene Carbonate
FE-SEM:	Field Emission Scanning Electron Microscopy
FSCs:	Flexible Supercapacitors
GCD:	Galvanostatic Charge Discharge
GPEs:	Gel Polymer Electrolytes
HR-TEM:	High Resolution Transmission Electron Microscopy
HQ:	Hydroquinone

IC:	Indigo Carmine
ILs:	Ionic Liquids
LICs:	Lithium-ion Capacitors
NMP:	N-methyl Pyrrolidone
PCs:	Pseudo Capacitors
SSC:	Symmetric Supercapacitor
SCs:	Supercapacitors
TGA:	Thermogravimetric Analysis
Tg:	Glass Transition Temperature
XRD:	X-ray Diffraction

ABSTRACT

Full Name : [Abubakar Dahiru Shuaibu]

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Currently, fossil fuels play a dominant role in global energy production, accounting for over 80% of the world's energy output. However, their use is associated with significant environmental consequences, notably the emission of harmful greenhouse gases. To address the escalating energy needs and combat the challenges associated with climate change, there is an increasing demand for renewable energy sources. Securing cost-effective and appropriate material stands as a critical and formidable prerequisite in the development of supercapacitors. In this context, carbon derived from biomass through the processes of pyrolysis and chemical activation emerges as an excellent electrode material suitable for supercapacitors. Additionally, gel polymer electrolytes with superior ionic conductivity, robust mechanical strength and expanded voltage window are necessary for the development of high performance supercapacitors. This research focusses on the development of high performance supercapacitors by capitalizing on abundant resources such as date stone biomass, to produce a cheaper and environmentally benign electrochemical energy storage devices. In addition, the research do not only aid in waste management, but also serve as an economical platform for sustainable energy production technologies. Conclusively, the research presents a promising approach for the development of sustainable and eco-benign materials for energy storage applications. The use of date stone waste as a precursor material for activated carbon electrodes presents an opportunity for cost-effective and sustainable energy storage. Overall, the findings of this research have important implications for the future design and fabrication of high-performance and cost-effective supercapacitors.

ملخص الرسالة

الاسم الكامل: أبو بكر ضاهر شعيبو

عنوان الرسالة: واجهة إلكترونية محسنة للتأزر لتطبيق المكثفات الفائقة ذات كثافة الطاقة العالية

التخصص: علوم وهندسة المواد

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حالياً، تلعب الوقود الأحفوري دوراً سائداً في إنتاج الطاقة العالمي، حيث تسهم بأكثر من 80٪ من إنتاج الطاقة العالمي. ومع ذلك، فإن استخدامها مرتبط بعواقب بيئية هامة، لا سيما انبعاث الغازات الضارة من الغازات الدفيئة. للتعامل مع الاحتياجات المتزايدة للطاقة ومواجهة التحديات المرتبطة بتغير المناخ، هناك طلب متزايد على مصادر الطاقة المتجددة. تأمين مواد فعالة من حيث التكلفة والمناسبة يعتبر شرطاً حاسماً ومهماً في تطوير السوبركاباستورز. في هذا السياق، ينبع الكربون المستمد من الكتلة الحيوية من خلال عمليات التجفيف والتنشيط الكيميائي كمادة كهربية ممتازة ملائمة للسوبركاباستورز. بالإضافة إلى ذلك، فإن الكتل البوليمرية للجيل تتمتع بقدرة أيونية متفوقة وقوة ميكانيكية قوية ونطاق جهد متوسع ضرورية لتطوير سوبركاباستورز عالية الأداء. تركز هذه البحث على تطوير سوبركاباستورز عالية الأداء من خلال الاستفادة من موارد وفيرة مثل كتلة حجر التمر، لإنتاج أجهزة تخزين الطاقة الكهروكيميائية بتكلفة أقل وصديقة للبيئة. بالإضافة إلى ذلك، لا تساعد البحوث فقط في إدارة النفايات، بل تعمل أيضاً كمنصة اقتصادية لتقنيات إنتاج الطاقة المستدامة. في الختام، يقدم البحث نهجاً واعداً لتطوير مواد مستدامة وصديقة للبيئة لتطبيقات تخزين الطاقة. إن استخدام نفايات حجر التمر كمادة سابقة لأقطاب الكربون المنشطة يمثل فرصة لتخزين الطاقة بتكلفة فعالة ومستدامة. بشكل عام، تحمل نتائج هذا البحث أثراً هاماً على تصميم وتصنيع سوبركاباستورز عالية الأداء وفعالة من حيث التكلفة في المستقبل.

CHAPTER 1

INTRODUCTION

1.1 Background

Supercapacitors, which are promising electrochemical energy storage and conversion devices, have garnered significant attention from both industry and academia due to their exceptional benefits, including rapid charge/discharge and long cycle life, as well as high power density [1], [2], [3]. However, when compared to Li-ion batteries, supercapacitors have a relatively low energy density, with commercially available models providing just about 5-7 Wh/kg of energy density, which falls short of the growing need for high energy [4]. As a result, current research focuses on addressing the low energy density issue by improving the specific capacitance (C) and/or operating voltage (V) of supercapacitors according to the formula; $E = 0.5 CV^2$, where C is the Specific capacitance, and V is the working voltage of the supercapacitor [5]. Supercapacitors are categorized into three types based on their electrochemical energy storage mechanism: electrochemical double-layer supercapacitors (EDLC), pseudocapacitors, and hybrid supercapacitors. EDLC functions by adsorbing and desorbing anions and cations of the electrolyte, creating a double layer in the interface area between the electrode and the electrolyte solution. In contrast, pseudocapacitors utilize reversible redox reactions between the electrode material and electrolyte for charge storage, which is why they are also referred to as faradaic supercapacitors. Hybrid supercapacitors, on the other hand, employ both the EDLC and pseudocapacitor mechanisms to store energy [6]. As a result, hybrid supercapacitors possess a significant advantage in that they combine the favorable characteristics of both EDLC and pseudocapacitors. This leads to a high specific or areal capacitance, energy density, and power density [7]. Supercapacitors can be classified into two categories based on their fabrication method: symmetric and asymmetric supercapacitors. Symmetric supercapacitors consist of two identical electrodes (positive and negative), while asymmetric supercapacitors are made up of two dissimilar electrodes [8], [9]. Supercapacitors offer numerous benefits, such as high power density, fast charging time,

extended life cycle, low internal resistance, and environmental friendliness. Nonetheless, further research is necessary to enhance their performance and decrease the high cost of widespread application. The type of electrode materials used plays a significant role in improving the performance of supercapacitors and reducing their cost [10].

An approach to increase the specific capacitance is through the creation and production of pseudo capacitive electrode materials, such as transition metal oxides/hydroxides, metal chalcogenides, and conductive polymers with optimal structures and morphologies [1], [11], [12], [13], [14]. This is because pseudocapacitance is significantly higher than electric double-layer capacitance (EDLC) due to their different ways of storing charge. Recently, it has been discovered that by incorporating redox-active additives, such as KI [15], [16], [17], Na_2MoO_4 [18], [19], VOSO_4 [20], [21], hydroquinone [22], [23], [24], [25], $\text{K}_3[\text{Fe}(\text{CN})_6]$ [26], p-phenylenediamine [27], [28], and methylene blue [29], into electrolytes, pseudocapacitance can also be produced from redox reactions at the electrolyte/electrode interface. Compared to electrode material, achieving high pseudocapacitance in the electrolyte is easier and more cost-effective. Various electrode materials, including metal oxides, conductive polymers, carbon, and their composites, have been utilized in the manufacturing process of supercapacitors [30], [31], [32], [33], [34]. The advantageous properties of carbon make it a popular choice for use in EDLCs. Within the realm of supercapacitor research, diverse carbon-based materials have been explored, including graphene [35, p.], [36], graphite [36], carbon nanotubes [37], and carbon fibers [38]. In order to discover less expensive materials that exhibit environmentally-friendly properties, several carbon-based materials derived from biomass have been tested with positive results in the context of EDLCs [39]. These carbon materials were obtained from different kinds of biomass, including fruits ^[23], cherry stones [40], date stones [41], date leaves [42], jute sticks [43], [44], [45], leaves of tal palm [46], *Syzygium cummini* leaves [47], *Albizia procera* leaves [48], waste of tea leaves plants [49], and microorganisms [50]. Broadly speaking, the various techniques utilized to produce these carbon materials can be categorized as either pyrolysis heat treatments or activation processes [51]. The pyrolysis treatment of carbon involves the transformation of non-conductive carbon derived from biomass into a conductive carbon material that demonstrates advantageous properties for

implementation as an electrode material in diverse electrochemical applications, such as supercapacitors [30–32].

Palm date-derived carbon has been identified as a valuable material that can be obtained through the heat treatment of waste generated by palm trees. It is noteworthy that palm trees are significant to the agricultural and food industries in many countries worldwide. The carbon material derived from palm dates finds application in diverse fields such as adsorption [52], wastewater treatment [53], carbon dioxide capture [54], removal of phenolic pollutants [55], elimination of heavy metals and dyes [56], and as a filter aid in the food industry for sunflower oil purification [57]. The date palm (*Phoenix dactylifera*) is a flowering plant that belongs to the *Arecaceae* family, cultivated in tropical regions for its sweet, edible fruit [58]. Date seeds are ideal for synthesizing nano carbons and activated carbons owing to their remarkable structural organization, high lignocellulosic nature, and low ash content [59]. The composition of date seeds consists of 42% cellulose, 18% hemicellulose, 25% sugar and other compounds, 11% lignin, and 4% ash [60]. Notably, date seeds account for 11-18% of the total weight of a date fruit, with a significant proportion being discarded as waste. Only a small portion is utilized for animal feed, as documented in reference [27]. They are popular in the Middle East and are one of the most common agricultural by-products in the kingdom of Saudi Arabia (KSA). According to global statistics, KSA was the third-largest date producer in the world, with a production capacity of 0.9 million tons in 2019 [61]. Date seeds, like other biowastes, have been used to make activated carbon, but there has been little research and information on the potential of date seeds for energy storage applications. In the present study, date seeds were selected as a biowaste material for the preparation of carbon particles with porous structures, owing to their abundance, cost-effectiveness, and sustainability [41].

The electrolyte is a crucial component of supercapacitors, providing ionic conductivity and aiding in charge compensation of electrodes, ultimately determining the performance of the device alongside the electrode material [63]. Two essential factors of the electrolyte are its electrochemical stability window, which ensures that the electrode material remains free of decomposition reactions within the voltage range of the SCs, and its ionic conductivity, which affects the device's dynamic process and rate capability by

determining the number of carriers, ionic charge, and carrier mobility [64]. There are various types of SC electrolytes, such as aqueous, organic, ionic liquid, all-solid, gel, and redox electrolytes [65], with numerous previous reviews on the topic [66], [67], [68]. In terms of voltage, supercapacitors (SCs) utilizing ionic liquids (ILs) and organic electrolytes can offer a broad voltage range [69], [70]. However, the purification and assembly process for these electrolytes must be carefully carried out in a controlled environment to prevent contamination with moisture. Additionally, there are significant limitations to the practical use of these electrolytes, such as the flammability and explosion hazards of organic electrolytes, and the high cost and viscosity of ILs. Hence, aqueous electrolytes, which are cheap and don't require special conditions, are still considered a more viable option. Although, the voltage window of SCs using aqueous electrolytes is thermodynamically limited to 1.0 V due to water decomposition at 1.23 V [4], [71]. Fortunately, SCs using neutral aqueous electrolytes, particularly Li_2SO_4 , have a higher voltage window, reaching up to 2.2 V, thanks to the strong solvation of Li^+ cations and SO_4^{2-} anions [4]. On the other hand, the development of portable, wearable, and flexible electronic devices has led to increased interest in gel polymer electrolyte (GPE) based flexible supercapacitors (FSCs) in recent years [72], [73], [74]. GPEs serve not only as conducting media but also as separators in FSCs. They are usually composed of a liquid electrolyte and a polymer matrix, such as polyvinyl alcohol (PVA). PVA-based hydrogels are one of the most commonly used GPEs in FSCs due to their ease of preparation, non-toxicity, good film-forming properties, and low cost, but they have low ionic conductivity and poor mechanical strength [69], [75]. The addition of ionic liquids to GPEs has been found to improve ionic conductivity and mechanical strength due to the strong plasticizing effect of ionic liquids [75], [76]. Therefore, developing a superior PVA-based GPE that generates pseudocapacitance, has a wide voltage window, and excellent mechanical properties is a promising approach to achieve FSCs with high energy density. To date, no such GPE has been reported [77].

1.2 Basics of supercapacitor

Supercapacitors are different from traditional capacitors due to the absence of dielectric material. The charge storage mechanism in traditional capacitors is through

electrostatic charge separation, whereas supercapacitor consist of two electrodes separated by a separator immersed in an electrolyte solution. The charge storage mechanism in supercapacitors is due to polarization of ions within the electrolyte solution. Supercapacitors may be symmetric or asymmetric depending on the type of electrode material.

1.3 Energy storage mechanism in supercapacitors

Generally, there are three types of supercapacitors: EDLC, Pseudocapacitor, and Hybrid supercapacitor as shown in **Figure 1**. This classification is mainly based on the charge storage mechanisms.

- a) The EDLC capacitance is due to columbic charge separation at the electrode-electrolyte interface.
- b) Pseudocapacitance is due to a unique redox reaction.
- c) The combination of both mechanisms gives rise to hybrid supercapacitor.

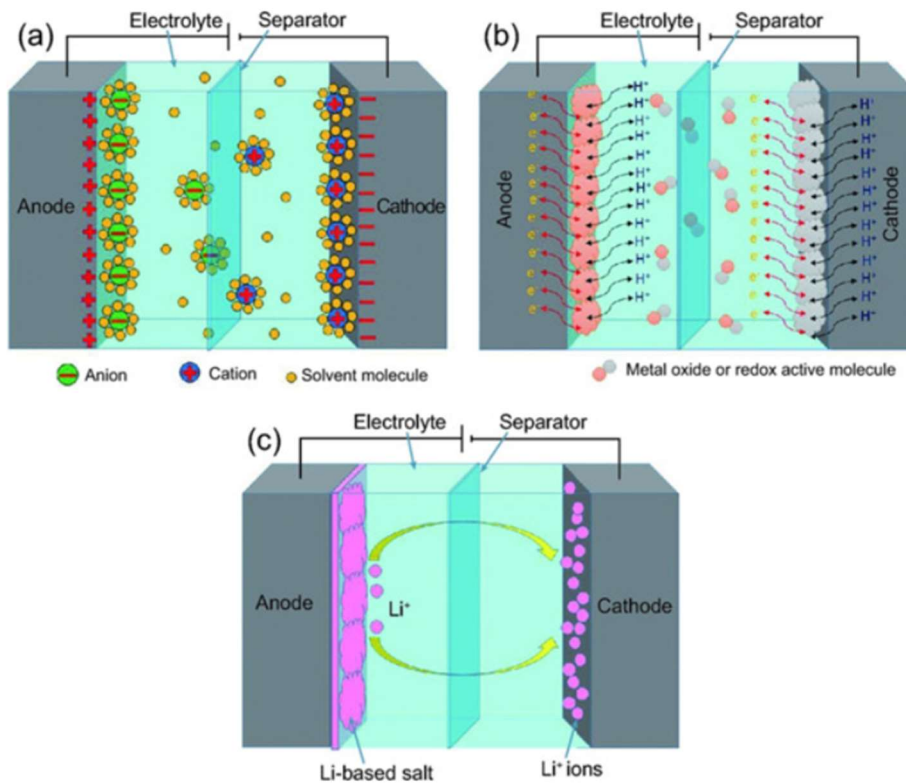


Figure 1. Classification of supercapacitors based on charge storage mechanism.

1.3.1 Electric Double Layer Capacitor (EDLC)

The operation of EDLCs is similar to that of conventional capacitors except for energy storage; which at the electrode-electrolyte interface [78]. In addition, these capacitors can store charge non-faradaically without any redox reaction. Therefore, no shifting of charge is allowed to happen at the interface [79]. Application of potential causes the charges to accumulate at the electrode surface. The charges are stored in the porous electrode through ion diffusion [80]. Ideally, the EDLCs stores charge by electrostatic charge distribution giving the capacitor high reversible nature as well as great stability without any change in volume [81], [82]. The capacitance of the EDLC can be calculated using equation (1) below.

$$C = \frac{\epsilon_0 A}{d} \quad (1)$$

Where ϵ_0 is the permittivity of free space, A is the electrode surface area, and d is the thickness of the double layer. The double layer thickness is inversely proportional to the capacitance and therefore should be kept very low. The charge transfer resistance of EDLCs is very low and as such they can attain long cycle life [83]. Most EDLCs uses carbonaceous materials such as activated carbon, carbon nanotubes, carbon aerogel etc. as electrodes [84]. These materials possess a large surface area, high conductivity and are chemically and mechanically stable. These materials are worthy of being utilized for the improvement of specific capacitance [83], [85].

1.3.2 Pseudocapacitors

Pseudocapacitors (PCs) lies at the interface between EDLC and battery. The charge storage mechanism in PCs involves a reversible redox reaction in addition to the faradaic charge storage mechanism of EDLC. An electron-charge transfer between the electrode and electrolyte caused by the de-solvated and adsorbed ions gives rise to the pseudocapacitance and usually, one electron per unit charge is involved [86]. Since PCs may store charge faradaically and involve a quick redox reaction between the electrodes and electrolyte, they are thought to be quite distinct from EDLCs [87]. Pseudocapacitance is greater than EDLC, but because of their weak electrical conductivity, they have low power density and insufficient cycle stability. The capacitance exceeds typical EDLC by

10-100 times [88]. Generally, the pseudocapacitance can be calculated using the below equation (2).

$$C = \frac{n \times F}{M \times V} \quad (2)$$

Where C is the capacitance, n is the number of transferred electrons, F is the faradaic constant, M is the molecular weight of the material, and V is the potential window.

Pseudocapacitance is attributed to a two-dimensional or almost two-dimensional charge storage mechanism as shown in **Figure 2**. Figure 2 shows three different charge storage mechanisms that contribute to pseudocapacitance [89]. Underpotential deposition results at higher potential relative to the Nernst potential. The deposition of a metal onto the surface of another metal occurs at higher potential compared to when it is deposited onto itself. The thickness of the deposit is not greater than a single layer. The fractional surface deposition occurs over a wide range of potentials. Electrosorption of lead on gold or hydrogen on platinum is a typical example of underpotential deposition [90]. The redox pseudocapacitance is because of redox reaction at the electrode-electrolyte interface which is usually faradaic in nature. The term redox stands for oxidation-reduction reactions. Oxidation involves loss of electrons while reduction occurs when electrons are gained. Ruthenium oxide was the first material to show supercapacitance, in this redox occur by accepting and releasing protons from and to the electrolyte solution. When it accepts protons, it also accepts electrons thereby changing its oxidation from +4 to +3 [91]. The term intercalation means insertion of positive ions into the porous electrode. There should be a controlled number of electrons transferred to the host during intercalation to maintain charge balance in the electrode [92].

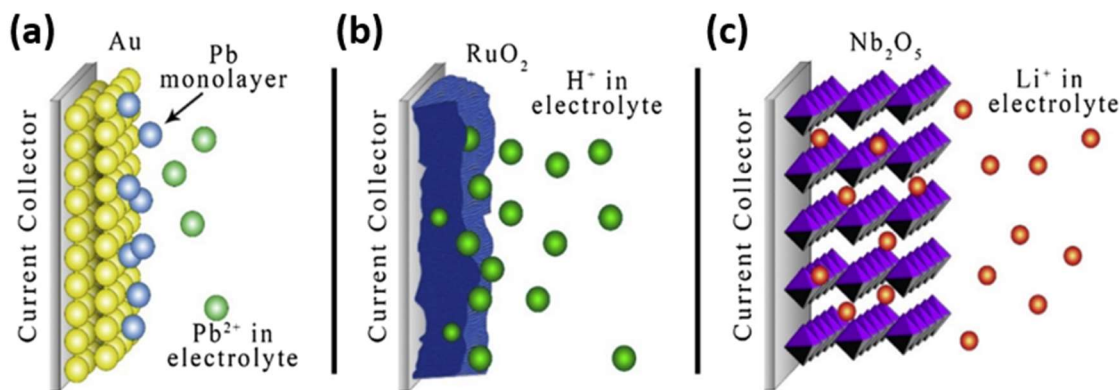


Figure 2. Different charge storage mechanisms that gives rise to pseudocapacitance: (a) underpotential deposition, (b) redox pseudocapacitance and (c) intercalation pseudocapacitance [89].

1.3.3 Hybrid supercapacitor

Hybrid supercapacitor and supercapattery are used interchangeably by researchers. The hybrid supercapacitor as the name implies is obtained by hybridization of the properties of EDLC and Pseudocapacitors. In other words, hybrid supercapacitor has the properties of both capacitors and batteries. To increase the energy density to about 20 to 30 W h kg⁻¹, the idea of hybrid supercapacitor was proposed [93]. The charge storage mechanism in hybrid supercapacitor is governed by combining the EDLC and Pseudocapacitor charge storage mechanisms. Pseudocapacitors do not have EDLC's limiting feature, and vice versa. When these two components are combined, the restrictions of the individual components are obscured, which has the benefit of delivering larger capacitance [94]. Hybrid supercapacitors can either be symmetric or asymmetric depending on the cell configuration. Symmetric is when both the electrodes are made from the same material. However, when the electrodes are made of different materials, it is called asymmetric. Asymmetric hybrid supercapacitors show better electrochemical performance than symmetric type [95].

CHAPTER 2

LITERATURE REVIEW

2.1 Electrode

In recent years, activated carbon derived from biowastes has drawn scientific interest for its potential use as a high-performance electrode material for energy storage devices, as well as in the domains of oil recovery[96], adsorption[97], separation[98], desalination[99], catalysis[100], and electrochemical sensors[46]. Numerous biomasses, including date leaves,[96] corn cobs,[101] *Butnea monosperma*,[102] and banana stems,[103] have been used in the physical or chemical carbonization and subsequent activation of holey carbonaceous materials.[104] The primary benefits of bio-waste-derived carbonaceous materials via pyrolysis are their environmental friendliness and cost-effectiveness. It is advisable to choose cost-effective activation methods for synthesizing carbon from biomass. However, it is important to note that the activation process may release unwanted gases, such as SO_2 and NO_2 , and caution should be exercised to avoid increasing the overall manufacturing cost by properly addressing these emissions.[105] Another advantage is that these biowastes are naturally occurring resources that are renewable and abundant.[104], [106] The use of biowastes in the fabrication of electrochemical supercapacitors (SCs) aids in waste disposal while also serving as an economic platform for sustainable energy storage technologies.[107]

2.2 Electrolyte

An essential component in energy storage systems is electrolyte, which plays a critical role in developing flexible, cost-effective, and high-performance supercapacitors (SCs). For an electrolyte to be considered ideal, it should possess certain characteristics such as eco-friendliness, good thermal and electrochemical stability, low toxicity, high ionic conductivity, a broad voltage operating window, as well as low volatility and flammability, as stated in references [43], [66], [108]. The electrolyte is a crucial component of supercapacitors, providing ionic conductivity and aiding in charge compensation of electrodes, ultimately determining the performance of the device

alongside the electrode material [63]. Two essential factors of the electrolyte are its electrochemical stability window, which ensures that the electrode material remains free of decomposition reactions within the potential range of the SCs, and its conduction of ions, which affects the device's dynamic process and rate capability by determining the number of carriers, ionic charge, and carrier mobility [64]. There are various types of SC electrolytes, such as aqueous, organic, ionic liquid, all-solid, gel, and redox electrolytes [65], with numerous previous reviews on the topic [66], [67], [68]. Redox electrolytes are a specific type of electrolyte that contains redox active species, which can significantly enhance the supercapacitors' electrochemical performance in two ways. Firstly, the electrolyte additive plays an active role in redox reactions during the charge and discharge processes of supercapacitors [109], [110], [111], [112]. Secondly, redox reactions in the electrolyte promote electron transfer between the electrode material and the redox species present in the electrolyte [113], [114], [115].

Ionic liquids consist of a large, asymmetric organic group and a weakly coordinating inorganic/organic group, which displays a broad working potential range (typically above 3.5 V), excellent cycle stability, and strong corrosion resistance, among other characteristics [116]. Quinones have been discovered as outstanding redox electrolyte additives in ionic liquid electrolytes in recent years. The incorporation of hydroquinone (HQ) [24], [117], [118] and benzoquinone (BQ)[119] into the electrolyte as organic redox shuttles results in low charge transfer resistance, which enhances the specific capacitance and specific energy of SCs. Furthermore, Lee et al. [120] state that adding tin sulfate and vanadium sulfate to the ionic liquid electrolyte can considerably enhance the overall performance of SCs. Xie H. J. et al. [121] synthesized two redox ionic liquids, [FcEIm][NTf₂] and [EMIm][FcNTf], by modifying either the [EMIm] cation or the [NTf₂] anion with ferrocene. Based on [EMIm][FcNTf], the energy density can reach as high as 13.2 Wh kg⁻¹, while a film deposited on the electrode prevents self-discharge at the cathode. It is apparent that redox-mediated ionic liquid electrolytes are a promising substitute for traditional electrolytes. However, liquid electrolyte leakage and oxidation in liquid electrolytes have significantly affect their application [122].

2.3 Gel polymer electrolyte

2.3.1 Structure of Gel polymer electrolyte and Mechanism of ion conduction

Sol undergoes a transition to a gel state upon the aggregation of its constituent particles to form a three-dimensional network. This phenomenon is referred to as the sol-gel transition and can be activated by increasing the concentration of the continuous phase or modifying temperature, among other factors. A gel is a solid-like material that comprises at least two components, one of them is liquid. The solid component represents the continuous phase, whereas the liquid component forms the discontinuous phase. Despite their liquid nature, gels exhibit solid-like attributes due to the extensive three-dimensional network that permeates the liquid medium [123], [124].

Gel polymer electrolytes (GPEs) are composed of a polymer network and solvents, wherein the polymer network envelops the liquid and impedes its escape (**Figure 3**). When water is used as the solvent, the resulting gel electrolyte is referred to as a hydrogel. Physical or chemical entanglements connect the polymer chains in GPEs, with physical gels employing electrostatic forces, hydrogen bonding, or chain entanglements to bind the polymer chains, while chemical gels rely on permanent covalent bonds to produce thermos-irreversible gels. The properties of polymer gels are contingent on the structure of the polymer network that forms the gel and the interaction of the network with the solvent. Gels are generally highly mobile due to the substantial amount of trapped solvent that solvates the polymer networks. In GPEs, the salt primarily provides free ions that participate in conduction enhancement, while the solvent aids in solvating the salt and serves as a conducting medium. Meanwhile, the polymer provides ideal mechanical stability by elevating the electrolyte's viscosity. In general, it is recommended to use salts with large anions and low dissociation energy and solvents with high dielectric constant, low viscosity, high boiling point, and low melting point [125], [126].

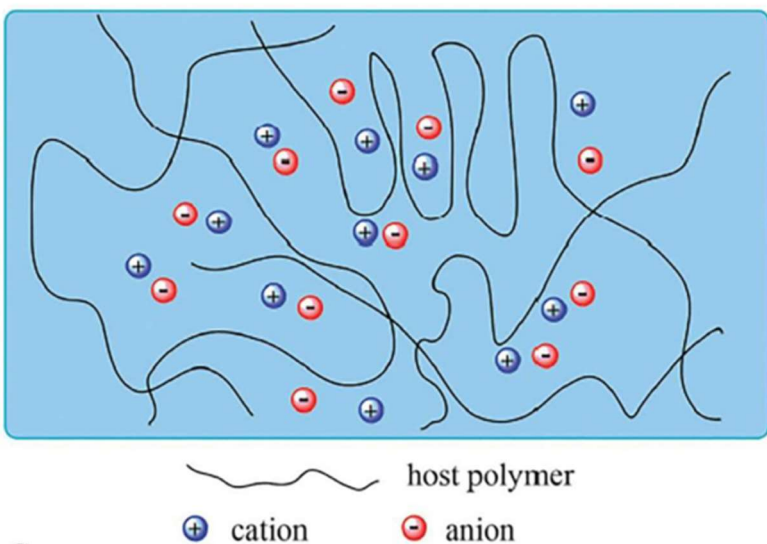


Figure 3. Schematic illustration of gel polymer electrolyte [66].

There are four distinct categories of gel polymer electrolytes (GPEs), namely (1) lithium-ion gel polymer electrolytes, (2) proton conducting gel polymer electrolytes, (3) alkaline gel polymer electrolytes, and (4) other ion gel polymer electrolytes. Lithium-ion gel polymer electrolytes are composed of a polymer, lithium salts, and organic solvents, which are commonly toxic, flammable, and expensive. Proton conducting polymer electrolytes are generated by mixing a polymer into a proton donor solution, such as $\text{H}_3\text{PO}_4/\text{H}_2\text{O}$. Protons are characterized by higher mobility compared to lithium ions and greater electrochemical stability than alkaline gels, rendering them a promising choice for ultrafast charge-discharge supercapacitors. Hence, proton conducting polymer electrolytes are deemed more advantageous as electrolytes owing to their higher ionic conductivity at room temperature and superior dimensional stability. Nonetheless, they do possess certain drawbacks, including limitations in operating temperature and narrower voltage windows due to the presence of water. Their superior proton conductivity is contingent upon the availability of water, restricting their use to temperatures lower than the boiling point of water. Therefore, comprehending the mechanisms of proton migration across a range of operating temperatures is crucial in developing a suitable proton conducting polymer electrolyte, as illustrated in **Figure 4** [127], [128], [129].

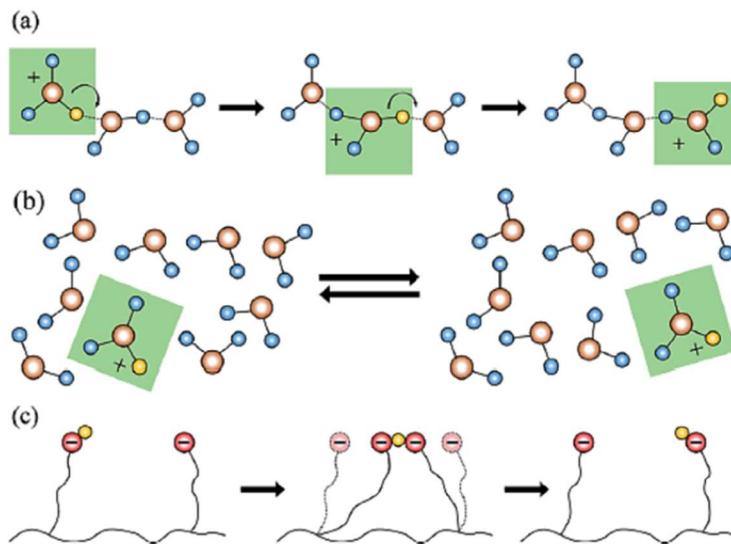


Figure 4. Schematic of a gel polymer electrolyte showing proton conduction mechanisms: (a) Grotthuss or hopping mechanism, (b) vehicle or diffusion mechanism, (c) segmental movement of protons through the polymer chains [130].

In the Grotthuss or hopping mechanism, the motion of protons is influenced by the rate of formation and cleavage of the hydrogen bond between the hydronium ion and the water molecule. A proton jumps from one site to another, each separated by a small energy barrier due to the formation of a strong hydrogen bond. Hence, low activation energy increases the mobility of the protons. In the diffusion mechanism, the proton forms a complex with water molecules and then penetrates. However, the penetration rate slows down due to the formation of hydrogen bonding with other water molecules. The proton penetration rate in this mechanism is slower than in the hopping mechanism and has a higher activation energy. In the direct transfer mechanism, the transfer occurs through the movement of polymer chains in the amorphous phase. The movement of the polymer chains in the amorphous phase facilitates the transfer of protons. The segmental motions of polymer chains can cause proton mobility in the amorphous phase above the glass transition temperature (T_g) of the polymer. The proton conduction mechanism is characterized as a function of temperature and increases with temperature and humidity. Consequently, the diffusion mechanism dominates the Grotthuss mechanism [128], [130], [131].

In the past few years, numerous polymer matrix materials have been investigated for the preparation of GPEs. These include poly(ethylene oxide) (PEO), poly(vinyl alcohol) (PVA), poly(methyl methacrylate) (PMMA), poly(acrylonitrile) (PAN), poly(vinylidene fluoride) (PVDF), and copolymer poly(vinylidene fluoride-hexafluoro propylene) (P(VDFHFP)) [69], [127], [132]. Poly (vinyl alcohol) (PVA) is a promising material for study due to its exceptional chemical stability, high mechanical strength, and ability to form transparent films. Additionally, PVA is non-toxic, making it an excellent candidate for various applications [77], [125], [133].

Based on the chemical composition and structure of the polymer network, the state of gel polymer electrolytes (GPEs) can range from a viscous liquid to a rigid solid. The ideal GPE should possess several desirable properties, such as a high ionic conductivity at room temperature, good mechanical strength, ease of thin-film formation, good electrode/electrolyte contact or adhesive properties, low cost, nontoxicity, compatibility with the electrode materials, low volatility, a wide potential window, excellent chemical, and thermal stability. The performance of GPEs is influenced by different factors, which vary depending on the composition of the GPEs. The properties of a gel electrolyte are determined by various factors such as the type of salt, ion size, concentration of salt and solvent, type of polymer and solvent (including dielectric constant and viscosity), and interactions between the polymer and other components. If water is used as the solvent, the resulting gel polymer electrolyte may exhibit poor mechanical strength and have a narrow range of operable temperatures. Gel polymer electrolytes (GPEs) typically incorporate organic solvents or their mixtures as plasticizers, which in turn affects the glass transition temperature of the gel. The plasticizers can be increased to dissociate the amorphous region and ion aggregates, leading to an increase in ionic conductivity. Consequently, ionic conduction occurs through the polymer chains, and the amorphous region's connected network enhances ion mobility and ionic conductivity. However, the interfacial resistance at the electrode/electrolyte interface and the electrode material's thickness restricts the ion diffusion rate or rate capability of GPEs. Additionally, the performance of GPEs is significantly influenced by various liquid electrolytes with different ionic conductivities, thermal stabilities, and electrochemical stabilities. GPEs encounter issues related to fluidity at high temperatures and low thermal stability. To enhance their performance at higher

temperatures, the host polymer is chemically cross-linked, and various fillers are added. Inorganic inert fillers with a high dielectric constant are utilized to prevent ion-association, which adversely affects ionic conductivity. Additionally, the size, shape, and volume fraction of the fillers have a significant impact on the mechanical and electrical properties of GPEs. Although studies have examined the effects of fillers on the ion transport, mechanisms of ionic conduction, and electrochemical and mechanical properties of composite gel electrolytes, a comprehensive understanding of these effects remains elusive [66], [127], [134].

2.4 Classification of gel polymer electrolyte based on composition

2.4.1 Aqueous Gel polymer electrolyte (Hydrogels)

Several investigations into hydrogel electrolytes for supercapacitor applications have highlighted PVA as an ideal polymer, owing to its remarkable chemical stability, non-toxicity, and biodegradability. PVA, a water-soluble polymer, is the most extensively produced synthetic resin globally. Unlike most vinyl polymers, PVA is not derived from the vinyl alcohol monomer due to its inherent instability. Instead, this polymer is synthesized by hydrolyzing vinyl acetate under alkaline conditions, and the complete or partial hydrolysis process removes the acetate groups from polyvinyl acetate. The degree of hydrolysis refers to the number of residual acetate groups remaining in the reaction. Simply put, the higher the degree of hydrolysis, the lower the number of acetate groups present in the polymer [135]. As a result, PVA is a linear polymer that contains smaller hydroxyl groups than the remaining acetate groups. These hydroxyl groups do not interfere with the formation of crystalline regions in the polymer. Instead, they can engage in hydrogen bonding with hydroxyl groups in other chains, which results in the arrangement of these chains in a crystal lattice. In PVA solutions, hydrogen bonding occurs not only within chains and between chains but also between water and polymer chains [136], [137]. Furthermore, the -OH groups present in PVA are capable of absorbing significant amounts of water, thereby enhancing the ionic conductivity of the electrolyte [125], [138], [139]. Jiang and colleagues have reported on the preparation of aqueous gels based on poly(vinyl alcohol) potassium borate (PVAPB) through electrodeposition (ED) method (**Figure 5**). The ED process is known for its high efficiency and is independent of the size and shape

of the device components. Supercapacitors that use the PVAPB gel electrolyte exhibited lower resistance, higher specific capacitance, and better rate performance compared to those using liquid electrolyte. The researchers found that a 0.9 M KCl solution had the highest specific capacitance ($52.7 \text{ F} \cdot \text{g}^{-1}$) among the supercapacitors using PVAPB gel electrolyte with lower KCl solutions. Moreover, the charge-discharge performance and internal resistance were improved, likely due to the higher ionic conductivity of the PVAPB gel electrolyte [140].

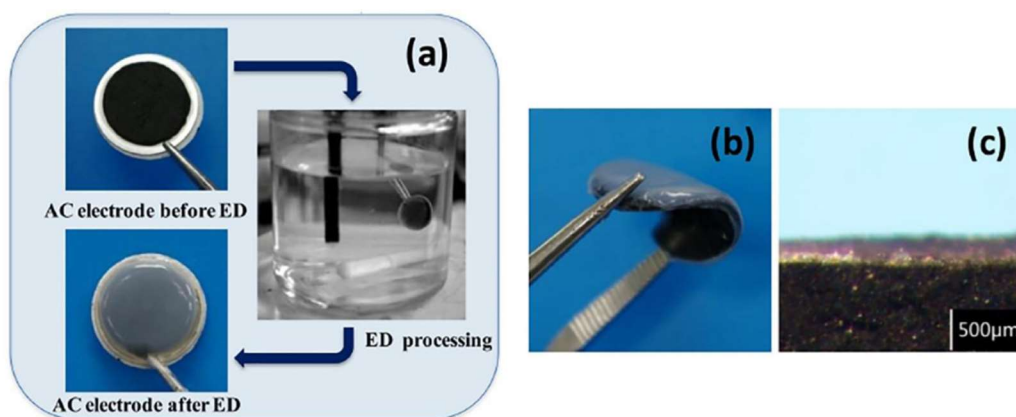


Figure 5. (a) AC electrode before and after electrodeposition of PVAPB GPE, (b) AC electrode coated with PVAPB GPE, (c) C-section of the AC electrode coated with PVAPB GPE [140].

Rosi et al. [138] have developed and characterized a hydrogel-based polymer electrolyte utilizing a PVA/H₂SO₄/H₂O system, along with the addition of hydroxyethylcellulose (HEC). Through the utilization of electrochemical impedance spectroscopy (EIS) and cyclic voltammetry tests, they have determined that the gel polymer electrolyte containing 1 wt% of HEC exhibits a notably low bulk resistance of 0.25Ω and a high capacitance of $160 \text{ F} \cdot \text{g}^{-1}$. The structural characterization of the gel polymer electrolyte was examined using Raman and Fourier transform infrared spectroscopy (FTIR). The FTIR spectrum indicated that HEC interacts with PVA/H₂SO₄ and forms a three-dimensional network to create a hydrogel. Huang et al. employed Raman spectroscopy to investigate the effect of gel electrolyte deformation on the arrangement of graphene oxide (GO) in hydrogels under tensile and compression tests. Their analysis

revealed that GO sheets align during the tensile process owing to the strong interaction between GO and boron-cross-linked PVA (B-PVA) systems (**Figure 6**) [141], [142].

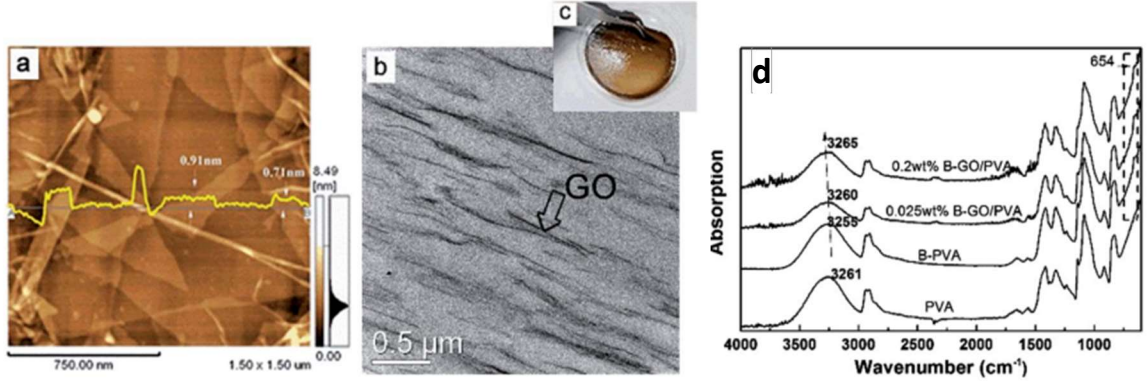


Figure 6. (a) AFM image of as-prepared GO sheets deposited on a mica substrate, (b) TEM image of dried 0.1 wt% B-GO/ PVA hydrogel, (c) 0.1 wt% B-GO/PVA hydrogel with ~95% water, (d) ATRFTIR spectra of dried PVA, B-PVA, 0.025 wt% B-GO/PVA and 0.2 wt% B-GO/ PVA hydrogels.

In general, two methods are commonly used to prepare supercapacitors using gel polymer electrolytes (GPEs). The first method involves preparing GPE films and then placing them between the electrodes. While this method is simple and produces flexible supercapacitors, the electrolyte may not fully penetrate the cracks in the electrodes, leading to high internal series resistance and low energy density. The second method involves preparing a gelable electrolyte solution and then adding it to the separator and electrodes to initiate the gelation reaction. This method ensures that the liquid gelable electrolyte solution can penetrate the cracks of the electrodes, thus significantly reducing electrode-electrolyte interfacial resistances. Moreover, this method improves the stability and durability of the entire system [140], [143], [144]. Pavani et al. have developed a gel electrolyte using PVA/KCl/H₂O at varying weight ratios of PVA/KCl. Polymer electrolytes typically comprise of crystalline and amorphous phases, with only the amorphous phase aiding in ion conduction. X-ray diffraction (XRD) analysis was utilized to investigate the impact of salt on polymer structure. A peak at 23.6° was observed for pure PVA, which was found to decrease with increasing salt concentration. This indicates that the crystallinity percentage of the polymer decreases with the addition of salt. Additionally,

the absence of salt peaks in the XRD spectrum confirmed complete dissolution of salt within the polymer matrix [145].

Wang and colleagues (**Figure 7**) synthesized an integrated supercapacitor by in situ polymerization of aniline in a gel electrolyte composed of PVA, H_2SO_4 , Glutaraldehyde, and H_2O at different aniline concentrations. SEM images revealed that polyaniline fibers were uniformly distributed and grown on the surface and edges of the gel electrolyte. Optical microscopy images demonstrated that polyaniline penetrated the electrolyte and formed a 250 micrometer-thick layer. The ionic conductivity of the gel electrolyte was measured at 0.082 S cm^{-2} . The resultant supercapacitor had a specific capacitance of 488 mF cm^{-2} , cyclic stability up to 7000 cycles, and a tensile strain of 300% [146].

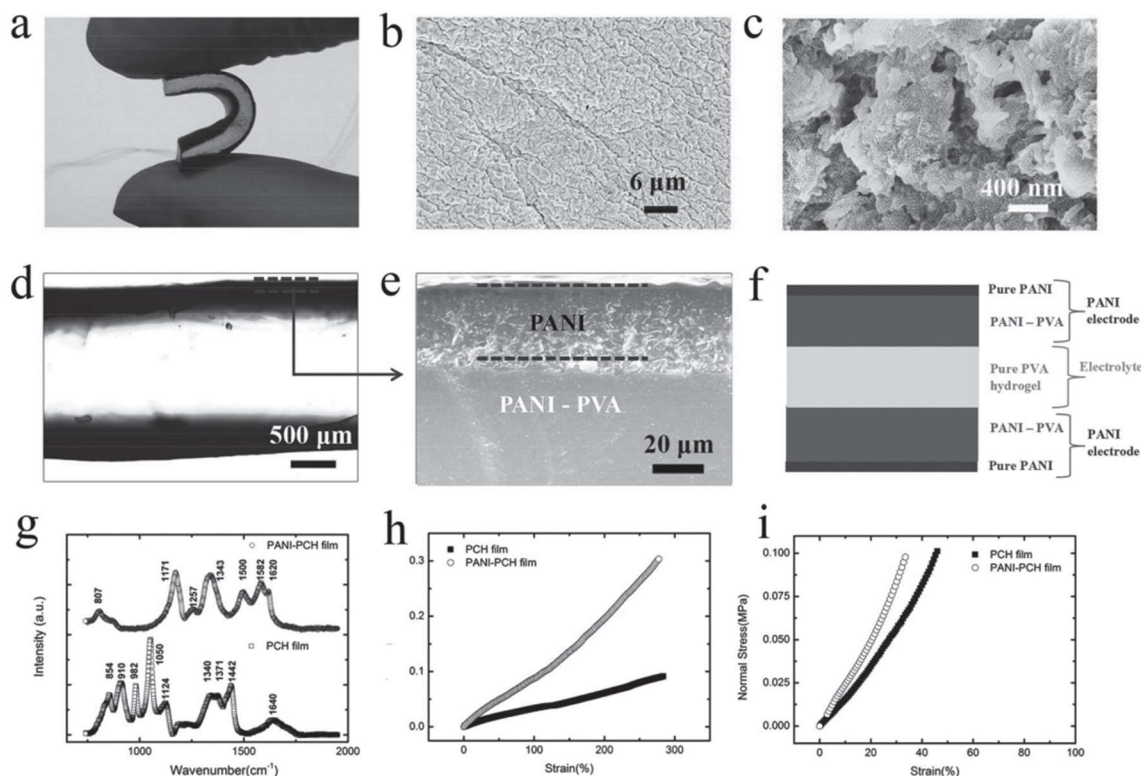


Figure 7. (a) PANI-PCH film, (b) SEM image of PANI-PCH film, (c) the enlarged SEM image, (d) Cross-section of PANI-PCH film by optical microscopy, (e) Cross-section of PANI-PCH film by cryogenic SEM performed at -130°C , (f) Schematic of the materials configuration in a single PANI-PCH film (g), Raman spectra, (h) Tensile stress-strain curves, (i) Compression stress-strain curves.

Table 1. Summary of Aqueous Gel Polymer Electrolytes (Hydrogels).

Electrolyte	Potential window (V)	Specific capacitance (F/g)	Energy density (Wh/kg)	Power density (W/kg)	Retention %/Cycle number	Reference
PVA/H ₂ SO ₄ /H ₂ O	1.0	147	12.6	1000	95/3000	[134]
PVA/H ₂ SO ₄ /H ₂ O	3.5	444	144	442	85.3/2000	[147]
PVA/H ₃ PO ₄ /H ₂ O	0.9	53	6	19200	100/1000	[148]
PVA/H ₃ PO ₄ /H ₂ O	0.6	99	24.12	78000	91/5000	[149]
SPI- Li ₂ SO ₄ -KI	1.5	224.19	16.02	573.78	58.21/1500	[150]
PVA-LiCl	2.0	82	48.5	2700	99/20000	[151]
CMC-Na/Na ₂ SO ₄	1.8	282	22.6	221	81.6/10000	[152]
PVA- Na ₂ SO ₄	1.5	138.1	15.09	2217.95	65.2/1000	[153]
PVA- Na ₂ SO ₄	1.6	90.6	32.2	3199.5	79.3/5000	[154]
PVA- Na ₂ SO ₄	1.7	168	67.4	850	93.4/5000	[155]
PVA- Na ₂ SO ₄	2.45	24.77	20.65	437.3	85.02/10000	[156]
PVA/KOH	1.4	68.93	29.97	38.89	76.68/1000	[157]
PVA/KOH	1.4	163.3	37.15	598.8	85.1/5000	[158]

PVA/KOH	1.4	316.6	29.33	42750	90.6/5000	[159]
Gelatin-ZnSO₄	1.8	138.5	110	20000	100/10000	[160]
PBI- H₃PO₄	1.0	52.5	5.85	1000	97.2/10000	[161]
PAA-Mo5	2.0	327.5	45.49	251.92	94/10000	[162]
PAA-Co7	1.5	341.33	21.25	117.69	92.7/10000	[163]
PVA/H₂SO₄	1.4	433	10.9	14014.5	91.25/5000	[164]
PVA/Na₂SO₄	2.45	430	20.65	437.3	82.75/10000	[156]

2.4.2 Gel polymer electrolytes made of organic solvents (Organogels)

To enhance the working cell voltage, research has been conducted on utilizing organogel electrolytes, which are gel polymer electrolytes (GPEs) based on organic solvents or plasticizers, as alternative electrolyte systems for energy storage systems (ESs). Different polymer hosts, including PEO [165], PMMA [166], polyvinylpyrrolidone (PVP) [167], PEEK [168], and various copolymers [169], [170], have been investigated in the literature as potential options for organogel electrolytes. These polymer hosts have been tested and studied in the context of organogel electrolytes. In a study by Hsueh et al. [169], a synergistic effect was observed between polyacrylonitrile (PAN) and polyethylene glycol (PEG) when used as the host for the gel polymer electrolyte (GPE). By adjusting the chain length ratio of acrylonitrile (AN) and ethylene glycol (EG) in the copolymer-based organogels, the ionic conductivity could be optimized. The maximum achieved ionic conductivity was $1.1 \times 10^{-2} \text{ S cm}^{-1}$, significantly higher than that of the $\text{LiClO}_4/\text{DMF}$ organic liquid electrolyte ($1.6 \times 10^{-3} \text{ S cm}^{-1}$). Carbon-based electric double-layer capacitors (EDLCs) utilizing this copolymer-based organogel electrolyte demonstrated higher energy and power densities (20 Wh kg^{-1} at 10 kW kg^{-1}) compared to EDLCs using organic liquid electrolytes. This suggests a positive synergistic effect between the PAN and PEG blocks in enhancing the performance of the EDLCs. Commonly studied organic solvents (plasticizers) in organogel electrolytes include PC, EC, DMC, and their mixtures, ACN, DMSO, and DMF. These systems have been extensively investigated in the research of organogel electrolytes. By employing these organogel electrolytes, the operating cell voltages of ESs were enhanced to 2.5-3 V, surpassing the values achieved by hydrogel electrolyte based ESs, including asymmetric configurations. This notable increase in cell voltages highlights one of the key advantages of organogel electrolyte based ESs. Consequently, the majority of reported organogel electrolyte based ESs exhibited relatively high maximum energy densities, ranging from approximately 18 to 25 Wh/kg. Notably, Schroeder et al. [171] demonstrated in **Figure 8** that a LIC (Lithium-ion capacitor) utilizing a methacrylate-based organogel electrolyte can be operated at an impressive cell voltage of 4 V. This achievement leads to a significant enhancement in energy density, showcasing the potential for further advancements in energy storage systems.

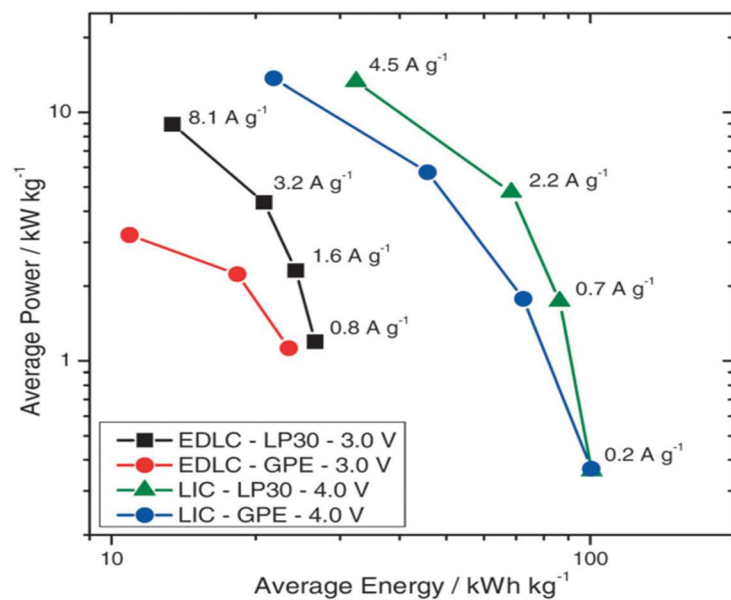


Figure 8. Ragone-like plot for two ESs and two LICs each containing either the liquid electrolyte LP30 or the methacrylate-based GPE.

Table 2. Summary of Organic solvent-based Gel Polymer Electrolytes (Organogels).

Electrolyte	Potential window (V)	Ionic conductivity (mS/cm)	Specific capacitance (F/g)	Energy density (Wh/kg)	Power density (W/kg)	Retention %/Cycle number	Reference
<i>p</i> FKM- <i>g</i> -PBA/Et ₄ NBF ₄ -AN	2.7	8.1	65.2	65.2	670	87/10000	[172]
PPDE-LiCl-EV	2.4	20	677	542	2880	85/2000	[173]
PVDF-HFP-LiClO ₄	1.0	4.27	74.41	10.33	4660		[174]
PVDF-HFP-LiPF ₆	3.7	2.07		180	218	97/100	[175]
PVDF-HFP-NaClO ₄	4.0		52.3	66-116	400-40000	82/4500	[176]
PVDF-HFP-NaClO ₄	3.0		65	13	200	71/5000	[177]
PVDF-HFP-NaClO ₄	2.0	2	150	17.7	14300	83/10000	[178]
PVDF(HFP)-PC-Mg(ClO ₄) ₂ -SiO ₂	1.5		442.3	101.6	2850	95/5000	[179]

2.4.3 Gel polymer electrolyte made of ionic liquids (Ionogels)

Ionic liquids (ILs) serve as plasticizing salts in GPEs, thereby enhancing the amorphous phase of the gels and improving their ionic conductivity, thermal stability, chemical stability, and mechanical properties. ILs are classified as room temperature molten salts with a melting point below 100°C, possessing exceptional characteristics such as non-volatility, non-flammability, excellent electrochemical and thermal stability, low vapor pressure, and a wide electrochemical potential window [180], [181], [182]. These remarkable attributes make them highly desirable for utilization in energy storage devices. Ionic liquids (ILs) are classified into three categories based on the specific combinations of anions and cations, namely aprotic, protic, and zwitterionic [183], [184], [185]. These categories of ILs have a wide range of applications in various fields, such as lithium batteries and supercapacitors for aprotic ILs, fuel cells for protic ILs, and membranes for zwitterionic ILs. ILs typically employ a range of cations and anions, including tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), bis(trifluoromethanesulfonyl)imide (TFSI^-), bis(fluorosulfonyl)imide (FSI^-), dicyanamide (DCA^-), imidazolium (EMIM^+), pyrrolidinium (PYR_{14}), ammonium (DEME^+), sulfonium (Me_3S^+), and phosphonium (P_{2224}). The hydrophilicity or hydrophobicity of the ILs is determined by the alkyl chain length on the cation and the specific anion used. For example, ILs based on (PF_6^-) are typically insoluble in water, whereas ethanoate-based ILs are fully soluble in water at room temperature. As a general trend, increasing the alkyl chain length results in decreased solubility in water [135].

Among the array of approaches available, the incorporation of ILs stands out as a potential means to improve the ionic conductivity of a GPEs. ILs possess compelling characteristics that render them viable and feasible for the synthesis of novel PEs. Their inherent high polarity and solubility towards an extensive range of ionic and organic compounds establish ILs as a promising candidate for ionic polymerization. The utilization of ILs in the preparation of Composite Polymer Electrolytes (CPEs) entails the function of IL as a solvent within the polymer chains of the electrolyte. The effectiveness of IL is reliant on several key factors, including the solubility of the IL monomer, the inherent mobility of the IL within the composite, and the charge density of the resultant hybrid materials [186]. The physical attributes of ILs, such as density, viscosity, hydrophobicity,

and melting point, are heavily influenced by the nature of their constituent cations and anions. The solubility of the ionic liquid, on the other hand, hinges on the size of the cations and counter anions, which may be organic or inorganic, with large-sized cations and smaller-sized anions being the favored combination [147], [187]. Anions possessing a bulky structure that facilitates charge delocalization are known to decrease the interaction between cations and anions in low lattice energy complexes [188]. Consequently, this promotes ionic dissociation and enhances the availability of mobile charge carriers for transportation, leading to an improvement in the ionic conductivity of IL-based GPEs [189].

The exceptional properties exhibited by ILs have garnered significant interest in recent years, primarily due to their versatility across a broad spectrum of applications. ILs find widespread use in several fields, including radical polymerization and catalytic cracking of polymers, among others [135]. Ionic liquid-based Composite Polymer Electrolytes (CPEs) present a viable alternative to traditional liquid electrolytes, owing to their environmental benefits. IL-CPEs are capable of eliminating the release of hazardous gases and solvents and can be recycled in specific applications [147]. The broad electrochemical potential window (typically above 3.5 V) exhibited by ILs has rendered them highly versatile in the field of electrical and electrochemical devices. In particular, Ionic liquid-based GPEs play a pivotal role in energy generation, storage, and conversion devices such as batteries, electrochemical actuators, electrochemical sensors, fuel cells, DSSCs, supercapacitors, and electrochromic windows [147], [190]. These applications have significant technological implications and underline the growing importance of ILs in the field of electrochemistry.

Table 3. Summary of Ionic Liquid Gel Polymer Electrolytes (Ionogels).

Electrolyte	Potential window (V)	Ionic conductivity (mS/cm)	Specific capacitance (F/g)	Energy density (Wh/kg)	Power density (W/kg)	Retention %/Cycle number	Reference
PVA-HMIMCl-KOH	1.6	2.82	668	22	1080	70.4/5000	[191]
PVA-CNTs-Li₂SO₄-BMIMBr	1.8	61.1	392.1	41.3	220.9	87.9/10000	[192]
LiTFSI/EMIMTFSI/MCM-41	3.0	4.91	90	112	1119	83/2000	[193]
PVDF-HFP/EMITFSI	2.0	2.4	126–146	18–21	110–190	88/10000	[194]
PVA-Na₂SO₄-Pyr₁₄Br	2.0	27.1	266.6	33	459.2	81/8000	[195]
PVDF-HFP/EMITFSI/KI/DPA	2.5	4.52	337	73.2	34800	80/6000	[196]
PVDF-HFP/EMITF/NH₄TF	1.6	13	106	6.95	2580	90/2000	[197]

2.4.4 Redox mediated gel polymer electrolytes

A recent scientific advancement has unveiled a novel strategy for supercapacitors, involving redox mediation. This groundbreaking technique demonstrates remarkable efficacy in augmenting the ionic conductivity of supercapacitors while concurrently yielding additional capacitance. This is achieved through the swift and reversible redox reactions facilitated by the introduction of a redox mediator [135], [198]. These redox additives include anthraquinone [41], indigo carmine (IC) [122], 2-mercaptopyridine (PySH) [199], 1-butyl-3-methylimidazolium iodide (BMIMI) [77], alizarin red S (ARS) [200], FeBr_3 [201], 1,4 Naphthoquinone [202], 1-anthraquinone sulfonic acid sodium (AQQS) [203] and 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM] BF_4) [204]. AD Shuaibu et al. unveiled a novel strategy involving redox mediation (**Figure 9**) by constructing a symmetric supercapacitor (SSC) using date stone-derived activated carbon (DSAC) and anthraquinone-based redox electrolyte. According to them, the date stone activated carbon was prepared by carbonization followed with activation using potassium hydroxide which gives a high surface area of $1612 \text{ m}^2/\text{g}$. The redox active gel electrolyte (PVA- H_2SO_4 -AQ) was prepared by solution casting method. An SSC device employing DSAC and PVA- H_2SO_4 -AQ delivered high specific capacitance of 126.5 F/g , high energy density of 17.5 Wh/kg at 250 W/kg . Moreover, the SSC device show remarkable performance with 87% capacitance retention after 1000 cycles. Finally, they concluded that the utilization of date stone waste in producing activated carbon electrodes not only offers a cost-effective solution but also aligns with sustainable energy storage practices [41].

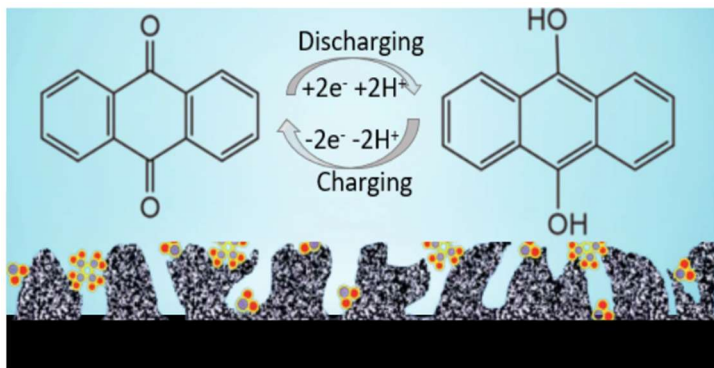


Figure 9. Reversible redox reaction of anthraquinone [41].

Feng et al. recently published a study detailing the addition of 1-antraquinone sulfonic acid, sodium (AQQS) to a polyvinyl alcohol-sulfuric acid (PVA-H₂SO₄) system, specifically in the form of a PH gel film. The elastic properties of the gel electrolyte and the fabricated supercapacitor are demonstrated in **Figure 10**. The findings indicate that the supercapacitor's capacitance remains remarkably stable even under various strain conditions when employing the gel electrolyte. The supercapacitor achieved a peak specific capacitance of 448 F g⁻¹ at a current density of 0.5 A g⁻¹.

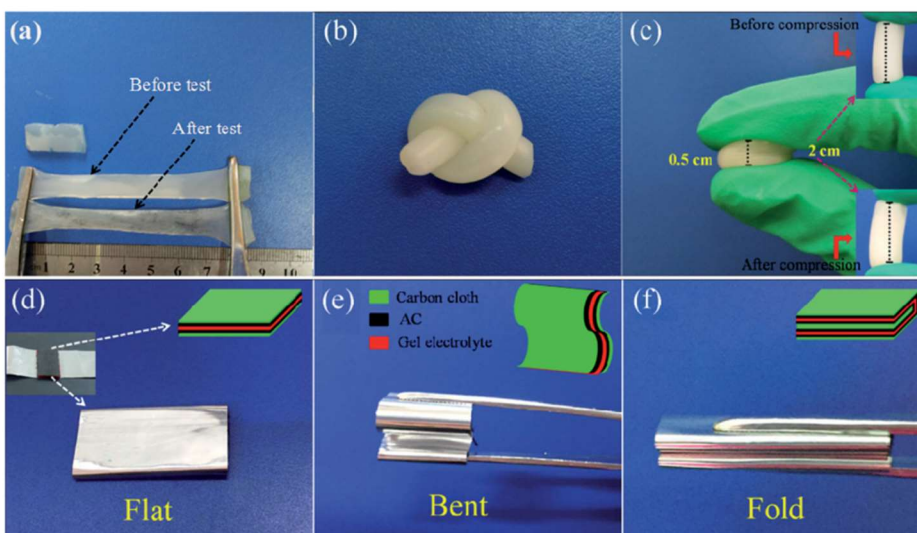


Figure 10. Elastic properties of PVA-H₂SO₄-AQQS gel electrolyte under different conditions, (a) stretching, (b) twisting, (c) compression.

Sun et al. have made significant advancements by developing a novel gel polymer electrolyte based on polyvinyl alcohol-hydrochloric acid-alizarin red S (PVA-H₂SO₄-ARS) system. This electrolyte formulation, represented as a flexible ribbon, exhibits impressive mechanical properties. It can be elastically stretched and released without any fracturing, and it can also be easily bent into spiral or circular shapes. The introduction of an optimized doping amount of alizarin red S (ARS) contributes to an enhanced ionic conductivity of 33.3 mS cm⁻¹ with the addition of 0.5 g of ARS. This increase in conductivity is attributed to the presence of hydroxyl groups (-OH) in ARS, making it soluble in water and acting as a plasticizer. Comparative studies between supercapacitors employing PVA-H₂SO₄-ARS electrolyte and PVA-H₂SO₄ electrolyte (without ARS) reveal notable differences in

performance. The supercapacitor utilizing the PVA-H₂SO₄-ARS electrolyte demonstrates a significantly higher specific capacitance of 441 F g⁻¹ compared to 160 F g⁻¹ exhibited by the counterpart with PVA-H₂SO₄ electrolyte, both evaluated at the same current density [200]. In a related study, Ma et al. have developed a supercapacitor by incorporating indigo carmine (IC) as a redox mediator into PVA-H₂SO₄ electrolyte systems. This supercapacitor showcases remarkable electrochemical performance attributes, including a high ionic conductivity of 20.27 mS cm⁻¹ with the addition of 0.1 g of IC. Additionally, it exhibits a high specific capacitance of 382 F g⁻¹, a high energy density of 13.26 Wh kg⁻¹, and an excellent cycle life, with the capacitance values maintaining 80.3% of the initial values even after 3000 cycles [122]. The experimental results presented in **Figure 13** demonstrate that the supercapacitors utilizing PHA gel films exhibit a significantly lower equivalent series resistance (ESR) value of 2.9 Ω·cm², confirming the enhanced ionic conductivity of the PHA gel film. The supercapacitor incorporating the PHA gel film exhibits a notably higher specific energy of 30.5 Wh·kg⁻¹ at a specific power of 350 W·kg⁻¹ [203].

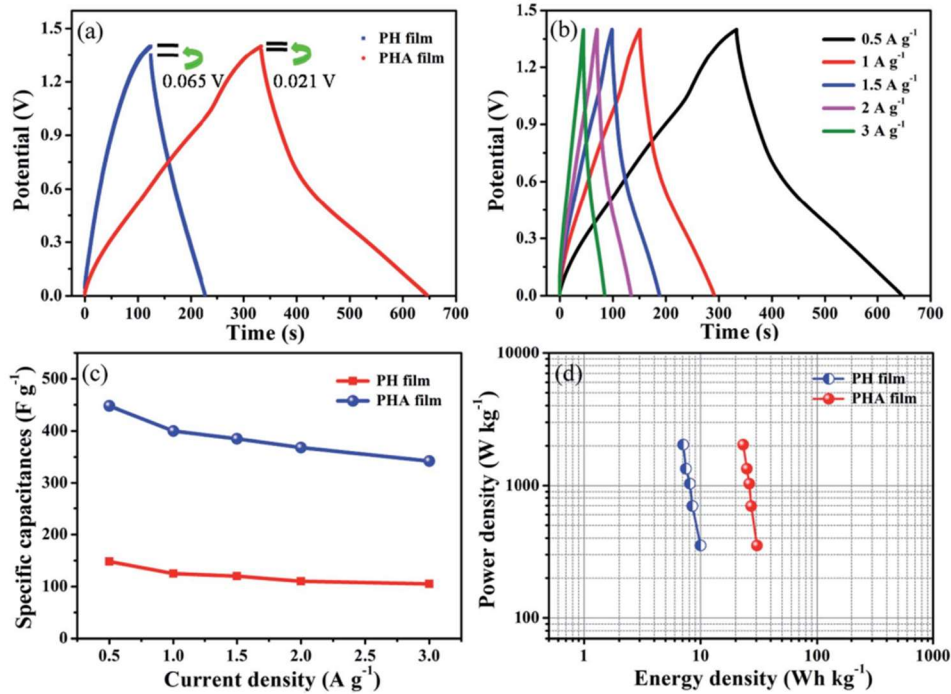


Figure 11. (a) GCD curves at a current density of 0.5 A g⁻¹, (b) GCD curves for PHA gel film at various current densities, (c) The specific capacitance (Cs) at different current densities, (d) Ragone plots.

Table 4. Summary of Redox mediated Gel Polymer Electrolyte.

Electrolyte	Potential window (V)	Ionic conductivity (mS/cm)	Specific capacitance (F/g)	Energy density (Wh/kg)	Power density (W/kg)	Retention %/Cycle number	Reference
PVA-H ₂ SO ₄ -ARS	1.6	33.3	441	39.4	400	78/1000	[200]
PVA-KOH-PNA	1.9	16.84	97.6	48.94	463.64	88.32/5000	[205]
PVA-KOH-KI	1.0	12.73	236.9	7.8	15.34	95.76/1000	[15]
PVA-KOH-KI	1.6	13.21	203.7	41.31	464.72	89.3/5000	[206]
PVA-KOH-PNA	1.8	16.84	161.77	72.79	727.96	90.74/5000	[207]
PVA-H ₂ SO ₄ -AQ	1.0		126.5	17.5	250	87/1000	[41]
PVA-H ₂ SO ₄ -VOSO ₄ /Na ₂ SO ₄	1.0	18.5, 31.1	543.4	17.9	13.9	80.4/3000	[111]
PVA-H ₂ SO ₄ -HQ/MB	1.0	29.3, 29.6	563.7	18.7	245	90/3000	[208]
PVA-KOH-PNA	1.9	16.84	97.6	48.94	463.64	88.32/5000	[205]
PVA-KOH-PNA	1.8	16.84	161.77	72.79	727.96	90.74/5000	[207]
PVA-KOH-KI	1.0	12.73	236.9	7.8	1534 0	95.76/1000	[15]
PVA/H ₂ SO ₄ /Na ₂ MoO ₄	1.0		95.14	13.2	625	98.2/5000	[209]

CHAPTER 3

High-performance Supercapacitors Enabled by Highly-porous Date Stone-Derived Activated Carbon and Organic Redox Gel Electrolyte

Abstract

Construction of eco-benign, cost effective, and high-performance supercapacitors with improved electrolytes and hierarchical porous electrodes is necessary for effective energy storage. In this study, a gel type organic redox electrolyte made of polyvinyl alcohol (PVA)-H₂SO₄ and an organic redox molecule, anthraquinone (PVA-H₂SO₄-AQ) was prepared by simple solution casting method and was used to construct a symmetric supercapacitor (SSC) with a date stone-derived activated carbon (DSAC) having a high BET surface area (1612 m²/g). The DSAC was synthesized by simple carbonization method followed by activation with potassium hydroxide. The SSC exhibit a high specific capacitance of 126.5 F/g at 0.5 A/g, as well as a high energy density of 17.5 Wh/kg at a power density of 250 W/kg with high capacitance retention (87%) after 1000 GCD cycles. The present research suggests that adding anthraquinone to a PVA-H₂SO₄ gel electrolyte improves the performance of the fabricated device significantly as compared to using pristine PVA-H₂SO₄ or 1M H₂SO₄ electrolytes. The research also presents a promising approach for the development of sustainable and eco-benign materials for energy storage applications. The use of date stone waste as a precursor material for activated carbon electrodes presents an opportunity for cost-effective and sustainable energy storage. Overall, the findings of this research have important implications for the future design and fabrication of high-performance and cost-effective supercapacitors.

3.1 Introduction

In recent years, activated carbon derived from biowastes has drawn scientific interest for its potential use as a high-performance electrode material for energy storage devices, as well as in the domains of oil recovery[96], adsorption[97], separation[98],

desalination[99], catalysis[100], and electrochemical sensors[46]. Numerous biomasses, including date leaves,[96] corn cobs,[101] *Butnea monosperma*,[102] and banana stems,[103] have been used in the physical or chemical carbonization and subsequent activation of holey carbonaceous materials.[104] The primary benefits of bio-waste-derived carbonaceous materials via pyrolysis are their environmental friendliness and cost-effectiveness. It is advisable to choose cost-effective activation methods for synthesizing carbon from biomass. However, it is important to note that the activation process may release unwanted gases, such as SO₂ and NO₂, and caution should be exercised to avoid increasing the overall manufacturing cost by properly addressing these emissions.[105] Another advantage is that these biowastes are naturally occurring resources that are renewable and abundant.[104], [106] The use of biowastes in the fabrication of electrochemical supercapacitors (SCs) aids in waste disposal while also serving as an economic platform for sustainable energy storage technologies.[107]

The world's use of energy has increased significantly as a result of rapid economic growth and population growth.[106] As a result, there is growing global interest in the issue of long-term sustainable energy production. In addition to cost and efficiency, one of the biggest challenges is energy storage. The successful use of recoverable energy necessitates energy storage after it is generated, which has prevented the widespread use of renewable energy including solar and wind energy.[12,13] Reliable electrical energy storage is the cornerstone of a quickly expanding market for portable electric structures and hybrid devices. As a result, SCs have attracted a lot of interest in the scholarly society.[14,15] SCs are widely acknowledged to be associated with low specific energy problems. However, when compared to rechargeable batteries, its rapid charging and discharging cycles are remarkable, which improves its ability to store an adequate amount of energy in a short amount of time.[214] The electrode is a critical components of the SCs because it affects the intrinsic efficiency of the SCs.[211] SCs can be designed for a variety of industrial applications by carefully selecting electrode materials and employing cost-effective preparation procedures.[43], [214]

Electrolyte is another important component of energy storage systems. It is critical in the development of cost-effective, flexible, and high-performance SCs. An ideal

electrolyte must be environmentally friendly, have good thermal and electrochemical stability, low toxicity, high ionic conductivity, a broad operating voltage window, and low volatility and flammability [18–20] Recently, an effective strategy for achieving high capacitance was proposed by incorporating redox-active species into gel-polymer electrolyte systems.[203] In this work, we have successfully prepared a gel-polymer electrolyte based on polyvinyl alcohol (PVA)-H₂SO₄ and anthraquinone as a redox additive.

In this study, we have chosen date seed as a biowaste to prepare carbon particles with porous structures because of its natural abundance, cost effectiveness, and sustainability. Dates (*Phoenix dactylifera*) are cultivated in the tropical region as a flowering plant that belongs to the palm family, Aceraceae, and are well known for their sweet edible fruit.[58] Date seeds are Ideal for synthesizing nano carbons and activated carbons owing to their remarkable structural organization, high lignocellulosic nature, and low ash content.[59] Their composition is 42% cellulose, 18% hemicellulose, 25% sugar and other compounds, 11% lignin, and 42% ash.[60] Date seeds account for 11–18% of the weight of the date fruit[62]. The date manufacturing industry produces a large amount of date seeds, but only a small portion of those seeds are used as cattle feed, with the majority being discarded as waste.[61] They are popular in the Middle East and are one of the most common agricultural by-products in the kingdom of Saudi Arabia (KSA). According to global statistics, KSA was the third-largest date producer in the world, with a production capacity of 0.9 million tons in 2019. [61] Date seeds, like other biowastes, have been used to make activated carbon, but there has been little research and information on the potential of date seeds for energy storage applications. As per our literature survey, there is no previous report on the preparation of a date stone-derived activated carbon having a high BET surface area for supercapacitor fabrication with a gel redox electrolyte.

Herein, we prepared activated carbon from date stones (DSAC) and used it to fabricate a symmetric supercapacitor (SSC) with a gel electrolyte made of PVA-H₂SO₄ and an organic molecule, anthraquinone (PVA-H₂SO₄-AQ), as a redox additive. The electrochemical properties of the SSC were thoroughly investigated using techniques, such as cyclic voltammetry (CV), galvanostatic charge-discharge cycle (GCD), and

electrochemical impedance spectroscopy (EIS). Moreover, we evaluate the performance of the SSC using PVA-H₂SO₄ without anthraquinone and 1.0 M H₂SO₄ electrolyte. The SSC performs admirably in the PVA-H₂SO₄-AQ, exhibiting a high energy density of 17.5 Whkg⁻¹ at a power density of 250 Wkg⁻¹ and a capacitance of 126.5 Fg⁻¹ at 0.5 Ag⁻¹. It also has excellent stability, retaining 87% of its capacitance after 1000 nonstop cycles.

3.2 Experimental

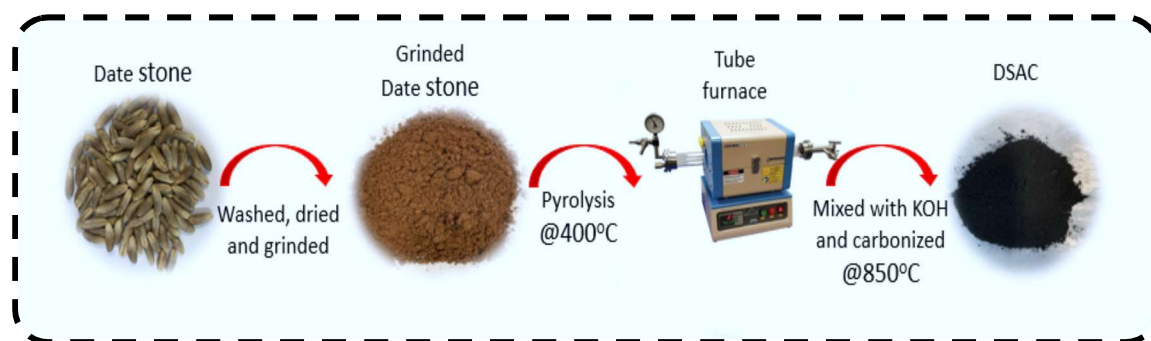
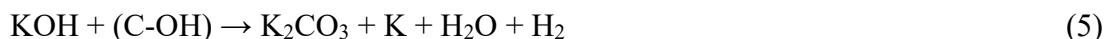
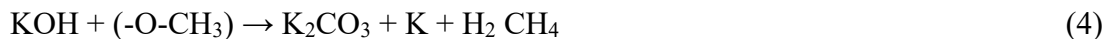
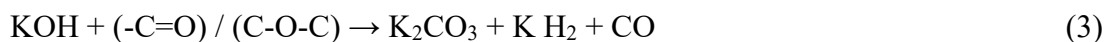
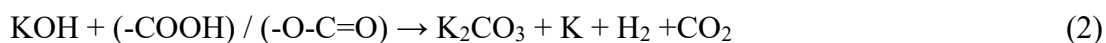
3.2.1 Materials

Date seed was obtained from a local source in Dhahran, Dammam, Eastern Province of KSA. Potassium hydroxide (KOH) pellets, H₂SO₄, polyvinyl alcohol (PVA), and anthraquinone were obtained from Sigma-Aldrich, while N-methylpyrrolidone (NMP)solvent, polyvinylidene fluoride (PVDF) binder, super conductive carbon, and stainless-steel foil were purchased from MTI corporation. High purity nitrogen gas was used during the synthesis of the activated carbon.

3.2.2 Preparation of activated carbon from date stones (DSAC)

The date stones were first thoroughly cleaned with distilled water multiple times to get rid of any contaminants, and they were then dried in an electric oven at 110 °C for 24 hours. With the use of a high-speed blender, the dried date stones were ground to powder. The resulting powder was carbonized in a furnace with a steady flow of nitrogen gas for three hours at 400 °C. The carbonization was carried out at a heating and cooling rate of 10 °C/min. and 5 °C/min. respectively. After that, the recovered carbon was thoroughly dissolved in a KOH solution that was constantly stirred. The reason why we chose KOH over chemical activating agents is because KOH is very promising due to its moderate activation temperature, higher biochar yields, and highly developed microporous structure with an ultrahigh specific surface area [216]. The carbon/KOH ratio utilized was 1:2. The resulting carbon solution was dried for a full day in an oven before being carbonized for three hours at 850 °C at a heating and cooling rate of 10 °C/min. and 5 °C/min. respectively under continuous nitrogen flow. The resulting activated carbon was then rinsed several times with 0.5 M HCl and then with hot deionized water to remove any residual KOH. A schematic illustration of the preparation of activated carbon is shown in **Scheme 1**.

The chemical activation mechanism using KOH can be summarized as follows: 1) carbon fragments are etched by KOH, K₂CO₃, and K₂O via the redox reaction; 2) gaseous products from the activation process further react with carbon; and 3) metallic Potassium (K) intercalates into the carbon framework and expand the carbon lattices, which results in a developed porosity. Thus, during biomass pyrolysis at lower temperatures, part of KOH can react with biomass via the chemical reaction between KOH and carbon fragments, generating H₂ and K₂CO₃ (Eq. (1)). Meanwhile, other more important reactions also occurred, i.e., KOH reacted with O-containing species to form H₂, CO, CO₂, CH₄, and K₂CO₃ (Eqs. (2-10)), especially at lower temperatures [216].



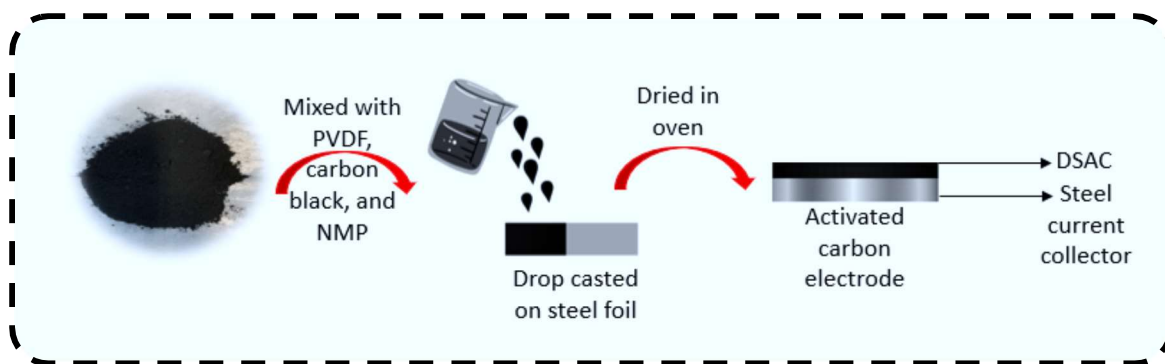
Scheme 1: Schematic representation for the preparation of activated carbon from date stones.

3.2.3 Characterization

The crystal structure and lattice characteristics were investigated using an X-ray diffractometer (XRD, Rigaku Miniflex-II diffractometer) and Cu-K-ray radiation at room temperature. The vibrational modes of the C-C bond stretching of the DSAC were examined using Raman spectroscopy. A HORIBA iHR320 spectrometer outfitted with a charge-coupled device detector and a 300 mW green light was used for the Raman analysis. The surface functional groups were determined using FT-IR spectroscopy. The sample was made up of ca. 100 mg of KBr and 0.5 mg of carbon, which was then compacted into pellets using a digital hydraulic press. The surface morphology of DSAC was examined using field emission electron microscopy (FE-SEM (JOEL, JSM6610LV)). Transmission electron microscopy (TEM) was used to examine the internal morphology and diffraction patterns of the DSAC (JOEL, JEM2100F). Grain lattice distortion and dispersion of grain boundaries were also investigated by TEM. Brunauer-Emmett-Teller (BET) was used to study the specific surface area, pore size distribution, and nitrogen adsorption/desorption isotherms. A Micromeritics ASAP 2020 surface area and porosity analyzer was used for the analysis. All electrochemical characterizations are conducted using the CHI 760E electrochemical workstation and at least each measurement was repeated three times to ensure that we obtained accurate results.

3.2.4 Fabrication of electrodes from the DSAC

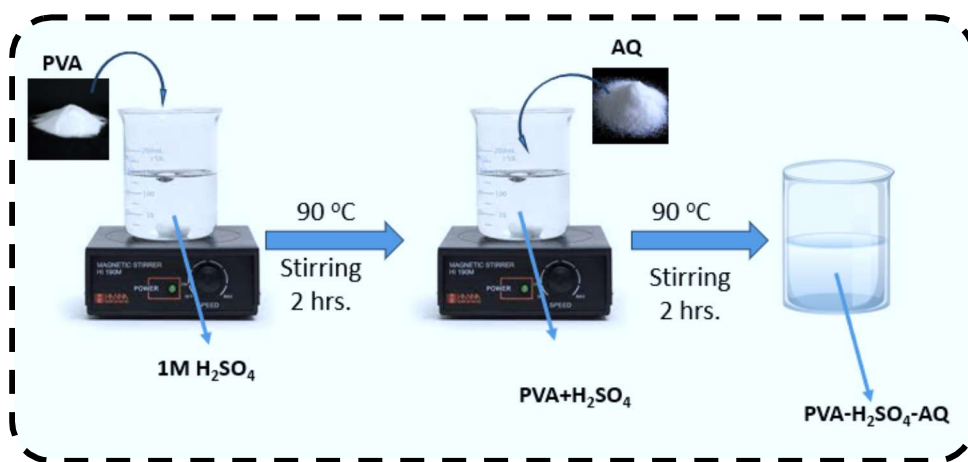
Activated carbon, Super P conductive carbon (with surface area of 63.2 m²/g), and PVDF binder were combined in a 75:15:10 ratio (w/w). The powder combination was ground in a mortar and pestle for 20 minutes to create a homogeneous mixture. To generate a thin slurry, the mixture was dissolved in the specified amount of NMP solvent and agitated at 90 °C for 4 hours. The slurry was then dropped cast on stainless steel foil. Each electrode contains roughly 0.7mg of the active substance (i.e. DSAC). This is illustrated schematically in **Scheme 2**.



Scheme 2: Schematic Illustration of the electrode fabrication process.

3.2.5 Preparation of the gel electrolyte (PVA-H₂SO₄-AQ)

With a few minor adjustments, the gel electrolyte was made using the method outlined in the literature [203]. Initially, 1.0 g of PVA was dissolved in 20 mL of a 1.0 M H₂SO₄ solution and stirred continuously for three hours at 90 °C to produce a clear viscous solution. To create the redox gel electrolyte, 0.1 g of anthraquinone was added to the aforementioned solution and stirred for an additional hour at the same temperature. Finally, the redox gel electrolyte was cooled to room temperature before using for SC fabrication. In comparison, PVA- H₂SO₄ without anthraquinone was produced using the same procedure. This procedure is illustrated schematically in **Scheme 3**.



Scheme 3: Schematic illustration of the synthesis route of the PVA-H₂SO₄-AQ electrolyte.

3.2.6 Electrochemical measurement

Scheme 2 depicts the electrode for the symmetric supercapacitor device. The developed SSC device was characterized using cyclic voltammetry (CV), galvanostatic charge/discharge (GDC), and AC impedance (EIS). The EIS measurement was performed at a frequency of 1 to 1 MHz. The prepared electrolyte-soaked filter paper served as the separator, and activated carbon served as the anode and cathode. Over a voltage window of 0 to 1.0 V, electrochemical measurements were conducted in a variety of electrolytes, including 1.0 M H₂SO₄, PVA- H₂SO₄, and PVA- H₂SO₄-AQ. Different scan rates ranging from 10 to 200 mVs⁻¹ were used for the CV measurement. Different current densities ranging from 0.5 to 5 Ag⁻¹ were used for the GCD approach. The stability of the manufactured SSC was tested in PVA- H₂SO₄ -AQ for 1000 GCD cycles. The precise capacitance, energy, and power of the SSC device were calculated from the GCD results using the equations (11-13) below:[217]

$$C(\text{F/g}) = \frac{I \times \Delta t}{m \times \Delta V} \quad (11)$$

$$E(\text{Wh/kg}) = \frac{1}{2} \frac{C \times \Delta V^2}{3.6} \quad (12)$$

$$P(\text{W/kg}) = \frac{E \times 3600}{t} \quad (13)$$

Where, I is the applied current, Δt is the discharge time, m is the mass of the active material on both electrodes, and ΔV is the operating voltage window, E is the specific energy (in Wh/kg), and P is the specific power (in W/kg).

3.3 Results and discussion

The XRD patterns of DSAC produced by carbonization in a tube furnace at 400 °C in an inert atmosphere and activation with KOH at 850 °C are shown in **Figure 12a**. The (002) planes of graphite correspond to broad patterns ranging from $2\theta=12^\circ$ to $2\theta=30^\circ$, with a peak at $2\theta=24^\circ$, indicating that the material is amorphous. A broad peak in XRD indicates that the material is amorphous, whereas a sharp peak denotes its crystalline nature. The XRD pattern of the DSAC also revealed a weak (101) peak with a 2-theta value at 44° caused by alpha-axis of the graphite structure.[218]

Raman spectroscopy can be used to determine the structure of carbonaceous materials, especially their graphitic and defective nature. The Raman spectra of the DSAC exhibits two distinct peaks (**Figure 12b**). The graphitic nature of the substance is represented by the G-band (at about 1600 cm^{-1}) and is connected to the E_{2g} vibrational mode of C-C (sp^2) bond stretching. On the other hand, an imperfect carbon structure with an A_{1g} vibrational mode is connected to the D-band (at about 1340 cm^{-1}). [219] The D-band is related to flaws, and its intensity increases as the number of defects increases. The I_D/I_G ratio provides information regarding the defects in carbonaceous material, with a high ratio indicating more defects in the carbon. [220] The measured I_D/I_G ratio of DSAC was 0.9. This low ratio indicates that the activated carbon has a good graphitic nature.

Figures 12c and 12d display N_2 adsorption/desorption isotherms and pore size distribution patterns of the DSAC. According to this information, BET surface area and pore volume of the DSAC are $1612\text{ m}^2/\text{g}$ and $0.692\text{ cm}^3/\text{g}$, respectively. The BET curve exhibited a type I-like isotherm, [43] which is typical of microporous materials with pore dimensions less than 2nm. The activated carbon exhibits meso- and macro-pores, as determined by the Barrett-Joyner-Halenda (BJH) pore size distribution analysis. These larger pores can enhance the transport of electrolyte ions through the carbon matrix, which is favorable for electrochemical energy storage applications. The presence of micro-pores, which dominate the high surface area of activated carbon, is also advantageous as it provides additional sites for electrolyte ion adsorption. As a result, the combination of micro-, meso-, and macro-pores in activated carbon can offer a favorable balance of surface area and ion transport properties that are well-suited for electrochemical energy storage applications. The result obtained from this analysis indicated that our activated carbon exhibits a high specific surface area which is comparable to the surface area of previously reported literatures as summarized in **Table 5** below.

The FTIR spectrum (**Figure 12e**) shows multiple peaks, however, the peaks at 1092 cm^{-1} , 1723 cm^{-1} , and 1458 cm^{-1} indicate the presence of C-O bonds and C=O bonds, respectively. [221] A peak at 1583 cm^{-1} indicates the presence of C=C bond. The peaks at 2852 cm^{-1} and 2922 cm^{-1} denote the C-H bond. On the other hand, a moisture-induced hydroxyl group can be detected in the broad peak at 3425 cm^{-1} . [221] These functional

groups and bonds are particularly prevalent in carbon generated from biomass. The presence of these types of oxygenated functional groups on the carbon improves supercapacitor performances by increasing the wet-ability of the carbon, allowing for easy electrolyte penetration.[42]

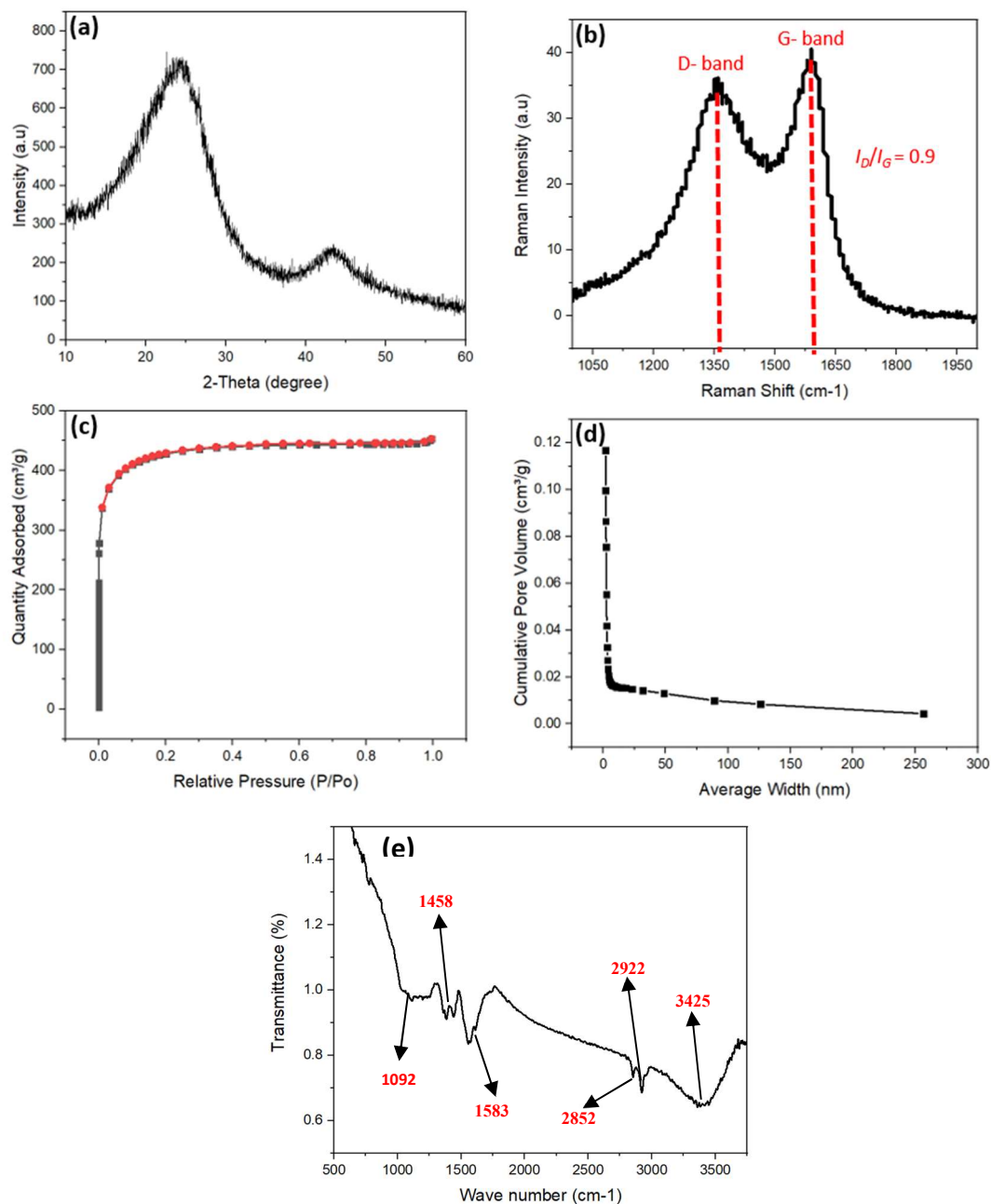


Figure 12. (a) XRD pattern, (b) Raman spectra, (c) nitrogen adsorption/ desorption isotherms, (d) BJH pore size distribution, and (e) FT-IR spectra of the DSAC.

Table 5: Comparison of the specific surface area and performance of DSAC with previously reported literature.

Activated carbon source	Activating agent	Surface area (m ² /g)	Electrolyte	Specific capacitance (F/g) @ 0.5 A/g	Specific energy (Wh/kg)	Specific power (W/kg)	Stability (%) / Cycles	Ref.
Jute sticks	NaHCO ₃	1100	KOH/ Glycerol gel	142	20	500	95/10000	[43]
Palm kernel shell	KOH	460	1M Na ₂ SO ₄	47	7.4	300	114/3500	[222]
Chinese fir	HCl	1873	1M H ₂ SO ₄	111	7.8	500	99.5/10000	[223]
Pinecone	KOH	1169.31	1M H ₂ SO ₄	44	16.1	457	96.1/10000	[224]
Ground coffee waste	KOH	1250	2M KOH	105.3	6.94	350	80/8000	[225]
Graphene foam	KOH	502	1M Na ₂ SO ₄	65	12	400	100/3000	[226]
Lima bean	KOH	1508	LiCl/PVA gel	119	4.13	5600	98/10000	[227]
Corn husk	KOH	1370	1M TEABF ₄ /AN	127	20	681	90/5000	[228]
Rice husk	KOH	2696	6M KOH	147	5.11	-	85/10000	[229]
Oil tea shell	ZnCl ₂	2851	1M KOH	146	24	275	81/3000	[230]
DSAC	KOH	1612	PVA-H₂SO₄-AQ gel	126.5	17.5	250	87/1000	This work

Figures 13a-c show FE-SEM images of the DSAC at different magnifications. Figure 13d shows the corresponding EDS elemental analysis. Figures 13a-c show that the activated carbon sample has a nanosheet-type morphology, with the sheets stacked on top

of each other to form a hierarchical 3-dimensional structure. The elemental composition of activated carbon was mainly carbon and oxygen, with trace amounts of potassium and magnesium. Copper substrate and gold coating caused Cu and Au peaks during the analysis.

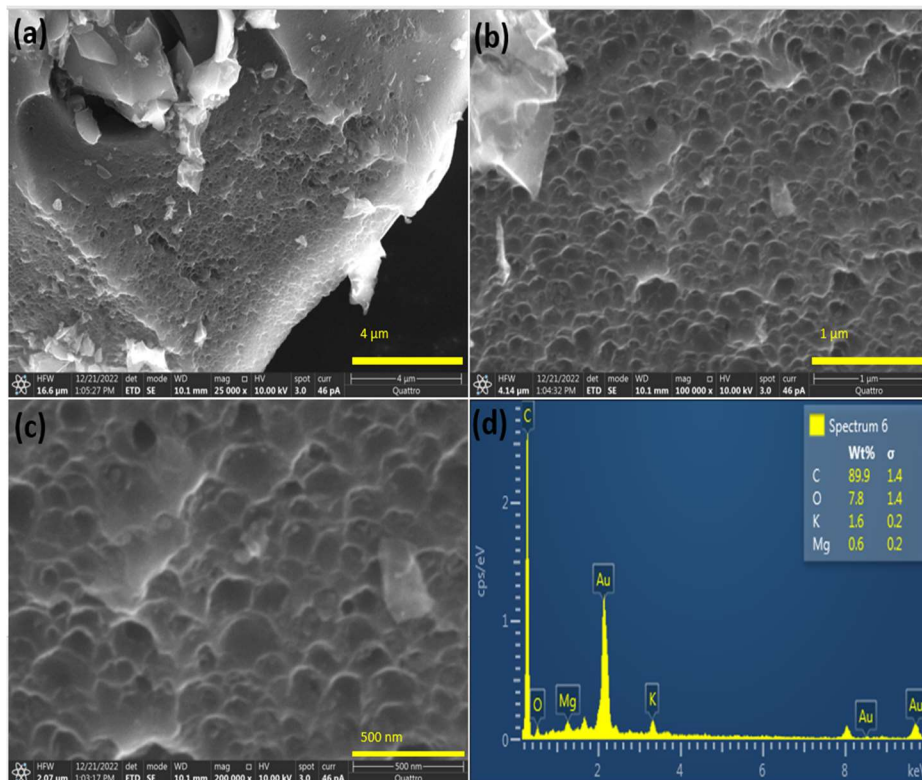


Figure 13: FE-SEM images of the DSAC (a-c) at different magnifications, (d) corresponding EDX spectra.

TEM spectra of the DSAC at different magnifications are shown in **Figures 14e-h**. As observed from **Figures 14e and f**, the DSAC exhibit a nanosheet-type morphology. High resolution transmission electron microscopy (HR-TEM; (**Figure 14g**)), and selected area electron diffraction (SAED; (**Figure 14h**)) results indicate that no lattice fringes were observed, confirming the amorphous nature of the material. These findings are consistent with the XRD analysis results.

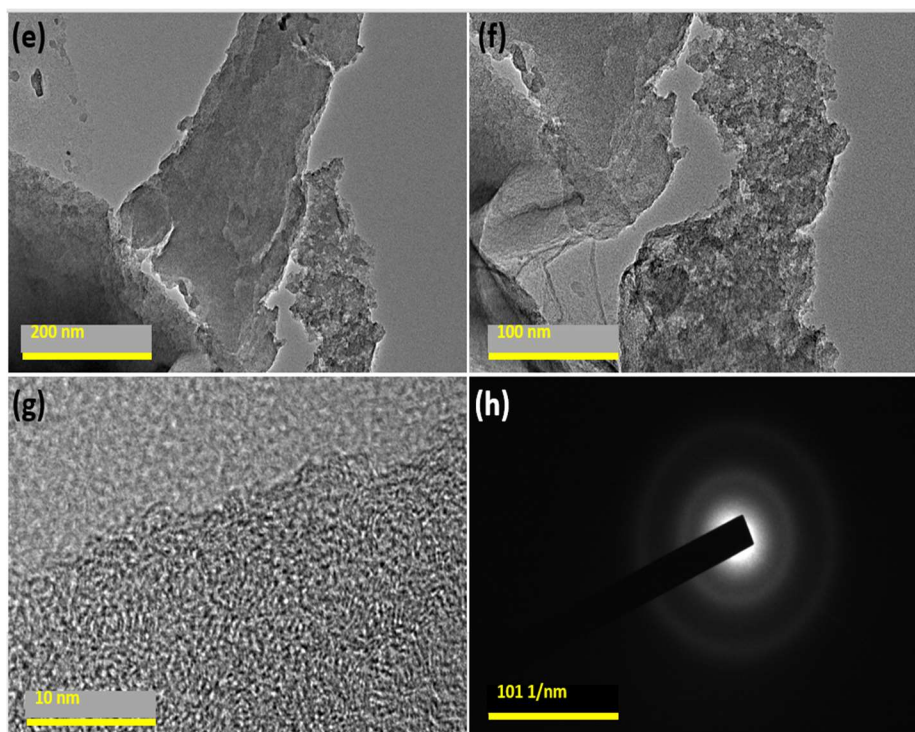
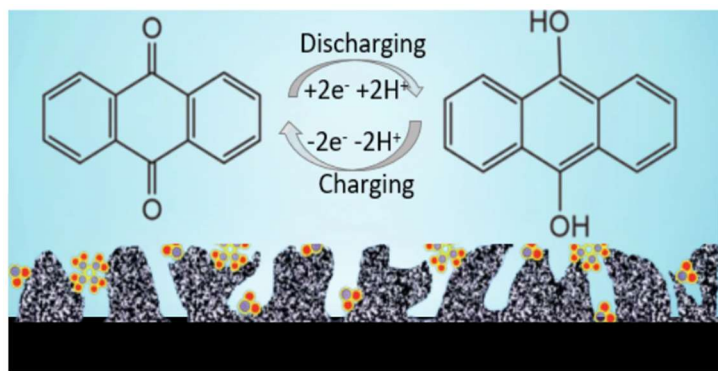


Figure 14: TEM spectra of the DSAC (e and f) at different magnification, and corresponding (g) HR-TEM, and (h) SAED.

3.4 Electrochemical Characterization

First, CV was used to characterize the electrochemical properties of the SSC device. **Figure 15a** displays the CV curves of the device using 1M H_2SO_4 , PVA- H_2SO_4 , gel polymer electrolytes, and PVA- H_2SO_4 -AQ gel-polymer electrolytes over a potential range of 0 to 1.0 V at a constant scan rate of 10 mV/s. The CV curves in all the electrolytes have a rectangular form, indicating that electric double layer capacitor (EDLCs), which store electrochemical energy by building up electrolyte ions at the electrode/electrolyte interface, have perfect behavior [203]. However, the curve in PVA- H_2SO_4 -AQ electrolyte exhibits a larger area, indicating that the electrolyte has a higher specific capacitance. At a scan rate of 10 mV/s, the specific capacitance calculated from the CV curves for the 1.0 M H_2SO_4 , PVA- H_2SO_4 , and PVA- H_2SO_4 -AQ gel-polymer electrolytes was 96, 130, and 185 F/g, respectively. This increased capacitance is attributed to the redox nature of the AQ (i.e. anthraquinone/9,10-dihydroxyanthracene redox couple) in the case of PVA- H_2SO_4 -AQ, as shown in **Scheme 4**.



Scheme 4: Redox nature of anthraquinone. [231]

The redox process becomes clear when the performance of a supercapacitor containing 1.0 M H₂SO₄ aqueous or PVA-H₂SO₄ gel-polymer electrolyte without the anthraquinone is compared. It can be concluded that the total capacitance of the supercapacitor with PVA-H₂SO₄-AQ gel electrolyte is the sum of the EDLC and the pseudocapacitance generated by the reversible redox reaction of anthraquinone at the electrode/electrolyte interface. **Figure 15b** depicts the CV curves of the SSC device using PVA-H₂SO₄-AQ gel electrolyte at various scan rates ranging from 10 to 200 mV/s. The values of the specific capacitance calculated from the CV curves are 185, 140, 131, 116, and 107 F/g at 10, 50, 100, 150, and 200 mV/s respectively. As usual, increasing the scan rate leads to a decrease in the specific capacitance. This is because the electrolyte ions have enough time to diffuse into the porous network of the activated carbon at low scan rates.

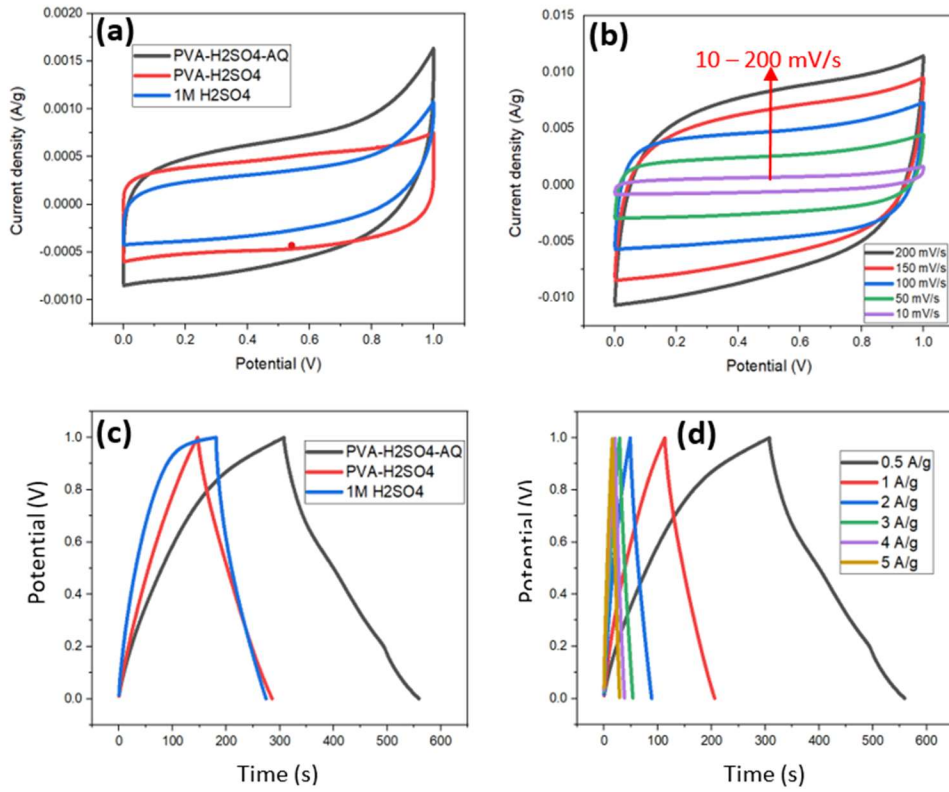


Figure 15: CV graphs of the SSC device (a) in different electrolytes at scan rate of 10 mV/s, (b) using PVA-H₂SO₄-AQ at different scan rates ranging from 10 to 200 mV/s, (c) comparison of GCD curves of the SSC device in a different electrolyte at a fixed current density of 0.5 A/g, and (d) GCD graphs of the SSC device using PVA-H₂SO₄-AQ gel electrolyte at different current densities.

Figure 15c compares the GCD curves of the SSC device in various electrolytes at a given current density of 0.5 A/g. **Figure 15d** shows the GCD curves for the SSC device using PVA-H₂SO₄-AQ gel electrolyte at various current densities ranging from 0.5 to 5 A/g. Equation (11) was used to calculate the capacitance of the SSC device at various current densities, and **Figure 16a** shows the result. Consistent with the CV data, the supercapacitor with the PVA-H₂SO₄-AQ gel electrolyte has a higher capacitance (i.e. a much longer discharge time) than the ones with the PVA-H₂SO₄ and 1M H₂SO₄ electrolytes at the same current densities. The specific capacitance of the supercapacitor with PVA-H₂SO₄-AQ is 126.5 F/g, which is substantially greater than that obtained with PVA-H₂SO₄ (72.5 F/g) and 1.0 M H₂SO₄ (47 F/g) at 0.5 A/g current density. This increased capacitance could be

due to the addition of the previously indicated rapid reversible redox mechanism of AQ. Equations (12 and 13) were used to determine the energy and power densities of the SSC device. **Figure 16b** depicts the E against P graphs (Ragone plots) of the SSC device. As per the plot, the supercapacitor exhibits the expected behavior, where an increase in power density leads to a reduction in energy density. **Figure 16c** displays the Nyquist plot obtained from the EIS measurements of the SSC device using various electrolytes. The electrolyte resistance R_b is indicated by the first intercept on the real axis in the high-frequency region, whereas the interfacial resistance is associated with the semicircle. [232] The equivalent series resistance (R_{ESR}) values of SCC using H_2SO_4 , PVA- H_2SO_4 , PVA- H_2SO_4 -AQ gel electrolyte systems were found to be 3.3, 5.3, and 0.5 Ω , respectively. The Figure shows that the SSC device based on the PVA- H_2SO_4 -AQ gel electrolyte has much lower charge transfer resistance, solution resistance, and diffusion resistance than the devices based on the other two electrolytes. **Figure 16d** depicts the Nyquist plot of the PVA- H_2SO_4 -AQ gel electrolyte-fabricated device before and after the stability test. According to the plot, there is no significant change in R_{ESR} . There is a significant increase in charge transfer resistance of the fabricated SSC and can be attributed to the degradation of the electrode due to the high current applied during the stability test. This shows that our fabricated SSC device exhibits robust performance.

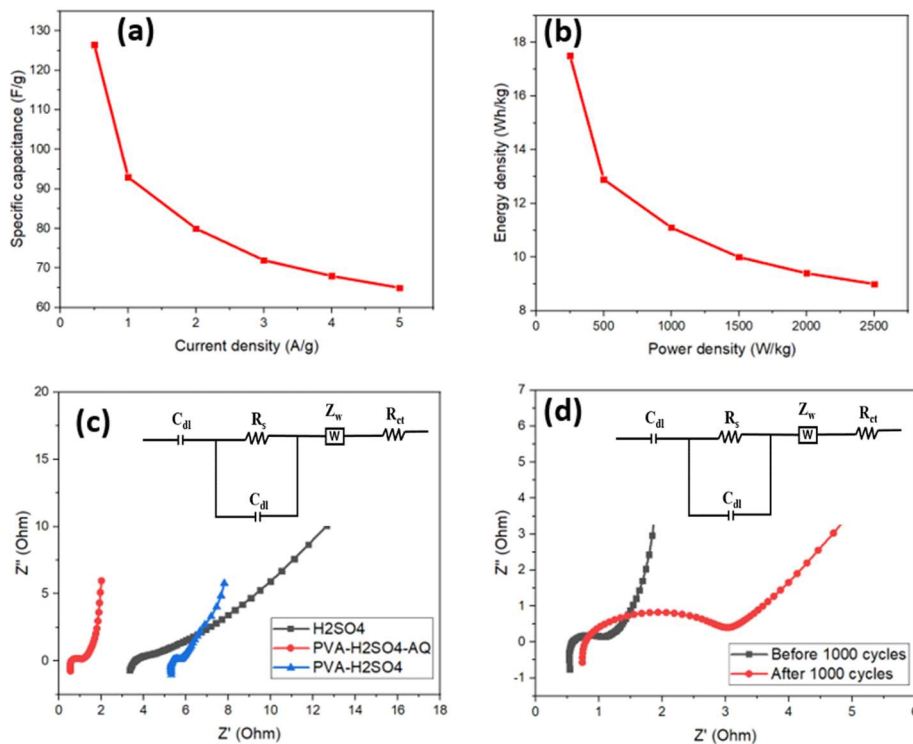


Figure 16: (a) Capacitance of the SSC device in different electrolytes at different current densities, (b) Ragone plot of the SSC device using different electrolytes, (c) Nyquist plot of the SSC device in different electrolytes, and (d) Nyquist plot of the SSC device before and after stability test (insert is the equivalent circuit model) .

3.5 Conclusion

Activated carbon was successfully prepared by simply carbonizing date stones and activating them with KOH. The results obtained from characterization of the activated carbon revealed that date stones have a great potential for electrochemical energy storage applications. Additionally, a symmetric supercapacitor was successfully constructed using the prepared carbon and anthraquinone-based redox gel electrolyte, and its electrochemical performance was investigated. The SSC displays impressive performance, with a high specific capacitance of 126.5 F/g, an energy density of 17.5 Wh/kg at a power density of 250 W/kg, and 87% capacitance retention after 1000 continuous GCD cycles, among other properties. To meet the growing demand for high-performance flexible energy storage devices, we developed a simple and effective method for fabricating supercapacitors using a strong redox-active gel polymer electrolyte and biomass-derived activated carbon.

CHAPTER 4

Development and Assessment of an Innovative Gel Electrolyte Using Polyvinyl Alcohol, Lithium Sulfate, and 1-Butyl-3-Methylimidazolium Trifluoromethanesulfonate for Advanced Supercapacitor Performance

Abstract

The quest for gel electrolytes with superior ionic conductivity, robust mechanical strength and expanded voltage window is an ongoing and significant area of interest. This study introduces a gel electrolyte, formulated from polyvinyl alcohol (PVA), lithium sulfate (Li_2SO_4), and 1-butyl-3-methylimidazolium trifluoromethanesulfonate (IL), termed PVA- Li_2SO_4 -IL. Developed through a straightforward solution casting and a freezing-thawing process, the incorporation of an ionic liquid into the gel polymer containing lithium salt enhances both the ionic conductivity of the electrolyte and imposes some pseudocapacitance to the supercapacitor. Comprehensive characterizations of the gel electrolyte's morphology, chemical composition, crystallinity, thermal stability, and mechanical attributes were conducted using various characterization techniques. Notably, the optimized gel electrolyte demonstrates a high ionic conductivity of 13.32 mS/cm at ambient temperature, improved to a peak conductivity of 31.42 mS/cm at 80 °C. When employed in a symmetric supercapacitor using activated carbon derived from date stones (DSCA) as electrodes, the supercapacitor achieves an exceptional energy density of 65.14 Wh/kg and high power density of 5000 W/kg. This energy density is attained due to the high operating potential window of 2 V and a notable specific capacitance of 117.25 F/g at a current density of 0.5 A/g. Furthermore, the supercapacitor exhibits remarkable cycling stability, maintaining 88.7% of its initial capacitance after 10000 cycles. These results position the PVA- Li_2SO_4 -IL gel electrolyte as a highly promising material for the advancement of high-power and high-energy-density energy storage systems.

4.1 Introduction

Supercapacitors, a promising class of electrochemical energy storage devices, have garnered significant attention from industry and academia due to their exceptional benefits, including rapid charge/discharge, long cycle life, and high power density [1], [2], [3]. However, compared to lithium-ion batteries, supercapacitors have a relatively lower energy density, with commercially available models providing just about 5-7 Wh/kg of energy density, which falls short of the growing need for high energy storage devices [4]. As a result, current research focuses on addressing the low energy density issue by improving the specific capacitance and operating potential window (OPW) of supercapacitors according to the formula: $E = 0.5 CV^2$, where C is the specific capacitance, and V is the OPW of the supercapacitor [5]. An approach to increase the specific capacitance is to create and produce pseudo-capacitive electrode materials, such as transition metal oxides/hydroxides, metal chalcogenides, and conductive polymers with optimal structures and morphologies [1], [11], [12], [13], [14]. This is because pseudocapacitance is significantly higher than electric double-layer capacitance (EDLC) due to their different ways of charge storing. In addition, the electrolyte can be modified to induce pseudocapacitance as well, as it has been discovered, recently, that by incorporating redox-active additives, such as KI [15], [16], [17], Na_2MoO_4 [18], [19], VOSO_4 [20], [21], anthraquinone [41], hydroquinone [22], [23], [24], [25], $\text{K}_3[\text{Fe}(\text{CN})_6]$ [26], *p*-phenylenediamine [27], [28], and methylene blue [29], into electrolytes, pseudocapacitance can also be produced from redox reactions at the electrolyte/electrode interface. Therefore, electrolyte engineering is a promising field to fabricate energy storage devices with high energy density.

The electrolyte is a crucial component of supercapacitors, providing ionic conductivity and aiding in charge compensation of electrodes, ultimately determining the device's performance alongside the electrode material [233]. Two essential factors of the electrolyte are its electrochemical stability window, which ensures that the electrode material remains free of decomposition reactions within the voltage range of the supercapacitors, and its ionic conductivity, which affects the device's dynamic process and rate capability by determining the number of carriers, ionic charge, and carrier mobility

[64]. There are various types of supercapacitor electrolytes, such as aqueous, organic, ionic liquids (ILs), all-solid, gel, and redox electrolytes [65], with numerous previous reviews on the topic [68], [234], [235]. In terms of voltage, supercapacitors utilizing ILs and organic electrolytes can offer a broad OPW range [29,32]. ILs consist of a large, asymmetric organic cation and a weakly coordinating inorganic/organic anion, which displays a wide OPW range (typically above 3.5 V), excellent electrochemical stability, and strong oxidation resistance, among other characteristics [33]. However, the purification and assembly process for these electrolytes must be carefully conducted in a controlled environment to prevent contamination with moisture. Additionally, there are significant limitations to the practical use of these electrolytes, such as the flammability and explosion hazards of organic electrolytes and the high cost and viscosity of ILs. Hence, aqueous electrolytes, which are cheap and do not require special conditions, are still considered a more viable option. However, the OPW of supercapacitors using aqueous electrolytes is practically limited to 1.0 V due to water decomposition at 1.23 V [4,34]. Fortunately, supercapacitors using neutral aqueous electrolytes, particularly Li_2SO_4 , have a higher OPW, thanks to the strong solvation of Li^+ cations and SO_4^{2-} anions [4].

The solution casting method is employed to create gel electrolytes. The main constituents of the solution system are polymer and solvent, although various additives such as acids, bases, and salts can also be incorporated. The selection of the polymer is crucial when formulating the casting solution. Specifically, the polymer must be soluble in the chosen solvent at an appropriate concentration and closely tied to the intended application of the final gel electrolyte. Lower polymer concentrations typically result in gel electrolytes with a porous structure, while higher polymer concentrations yield gel electrolytes with a denser structure [35]. The solvent selection is not random; instead, it is based on specific requirements. The solvent needs to have the ability to dissolve the polymer, as well as being miscible with a non-solvent when employed as a coagulation medium. Both kinetic and thermodynamic factors must be considered in this regard. When the aim is to obtain gel electrolytes with porous and asymmetric structures, aprotic solvents like dimethyl formamide, dimethyl acetamide, or dimethyl sulfoxide are preferred due to their rapid phase separation in water. Conversely, solvents that facilitate slow polymer precipitation, such as acetone or tetrahydrofuran, produce dense gel electrolytes [35]. By

incorporating different modifiers into the solution casting process, it becomes possible to tailor the gel electrolyte properties according to the desired final application. The casting solution can be enhanced with various additives, including cosolvents, non-solvents, and different types of fillers, such as pore-forming agents and cross-linking agents [36]. Despite being used in relatively low concentrations; these additives play a crucial role in determining the ultimate performance and applications of the resulting gel electrolyte. On the other hand, the development of portable, wearable, and flexible electronic devices has led to increased interest in gel polymer electrolyte (GPE) based flexible supercapacitors (FSCs) in recent years [37–39]. GPEs serve not only as conducting media but also as separators in FSCs, they usually comprise a liquid electrolyte and a polymer matrix, such as polyvinyl alcohol (PVA). PVA-based hydrogels are one of the most commonly used GPEs in FSCs due to their ease of preparation, non-toxicity, good film-forming properties, and low cost. Still, they have low ionic conductivity and poor mechanical strength [29,40]. The addition of ILs to GPEs has been found to improve ionic conductivity and mechanical strength due to the strong plasticizing effect of ILs [40,41]. Therefore, developing a superior PVA-based GPE that generates pseudocapacitance, has a wide OPW, and has excellent mechanical properties is a promising approach to achieving FSCs with high energy density. To date, no such GPE has been reported [42].

Herein, we developed a novel PVA–Li₂SO₄–IL gel polymer electrolyte with high ionic conductivity, expanded OPW, and enhanced mechanical properties, and improved electrochemical performance by solution casting method. The developed gel electrolyte was assembled with date stone activated carbon (DSAC) (with a high surface area of 1612 m²/g and pore volume of 0.692 cm³/g) to construct a symmetric supercapacitor. Due to the synergistic effect between the PVA–Li₂SO₄ and the IL, the electrolyte exhibits the highest ionic conductivity of 31.42 mS/cm at 80 °C, and the symmetric supercapacitor fabricated using the developed gel electrolyte exhibits a high energy density of 65.14 Wh/kg, at high power density of 500 W/kg, and maintain high energy density of 31.94 at high power density 5000 W/kg. Furthermore, it also shows high cycling stability with 88.7% capacitance retention and a Coulombic efficiency of approximately 100% after 10000 cycles.

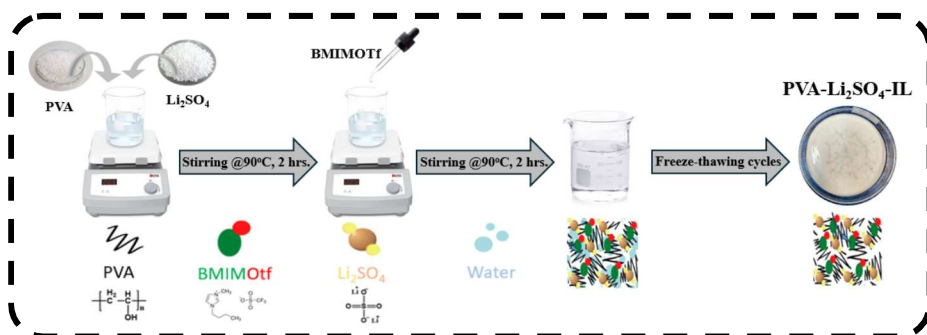
4.2 Experimental

4.2.1 Materials

Date stones were obtained from a local farm in Dhahran, Saudi Arabia. Potassium hydroxide (KOH) pellets, hydrochloric acid (HCl), Li_2SO_4 , PVA, and 1-butyl-3-methylimidazolium trifluoromethane sulfonate (BMIM Otf), were obtained from Sigma-Aldrich. At the same time, N-methyl pyrrolidone (NMP), polyvinylidene fluoride (PVDF), carbon black, and 304 stainless-steel foils were purchased from MTI corporation. Nitrogen gas of high purity was used to synthesize the activated carbon.

4.2.2 Preparation of the gel electrolyte (PVA- Li_2SO_4 -IL)

The synthesis of the gel electrolyte involved a straightforward solution casting technique, complemented by a freeze-thawing process. Initially, 2 g of PVA was dissolved in 20 mL of deionized water. This mixture was then heated to 90 °C under strong stirring until it formed a transparent, clear solution. Concurrently, 1 g of Li_2SO_4 was dissolved in another 20 mL of deionized water in a separate container. Once dissolved, this Li_2SO_4 solution was combined with the PVA solution. Following this, 2 g of the IL (BMIM Otf) was added to the mixture. The combined solution was continuously stirred until it reduced to approximately half of its original volume, becoming a sticky solution. This resultant solution was then poured into a glass petri dish. The dish was subjected to multiple cycles of freezing and thawing, leading to the formation of a free-standing, transparent, and flexible gel electrolyte. For comparative purposes, a PVA- Li_2SO_4 gel electrolyte without the IL was also prepared using a similar methodology. The detailed steps for the preparation of the gel electrolyte are illustratively represented in **Scheme 5**.



Scheme 5. Schematic illustration for the preparation of the gel electrolyte.

4.2.3 Preparation of DSAC

The preparation of date stone activated carbon (DSAC) was conducted as per the methodology outlined in our earlier publication [41]. The process commenced with the pre-carbonization of date stone powder. This powder then underwent an activation process using KOH. Following this, the material was subjected to a heat treatment at a temperature of 850 °C. This heating was conducted in an inert atmosphere, adhering to controlled heating and cooling rates of 10 °C/min and 5 °C/min, respectively, and was maintained for a duration of 3 hours. Post-heating, the carbon material was thoroughly washed with a 0.5 M HCl solution, which served to eliminate any residual KOH. This step was succeeded by an additional washing using deionized water to ensure complete removal of impurities. Finally, the carbon was dried in an oven, a process extended over 24 hours, to achieve the desired dryness and consistency for further use.

4.2.4 Fabrication of the supercapacitor device

The fabrication of the supercapacitor began with the preparation of electrodes. This process involved creating an ink by mixing DSAC, carbon black, and PVDF in a ratio of 7.5:1.5:1. NMP solvent was used to blend these components. The mixture was then subjected to magnetic stirring for one hour, resulting in a uniformly distributed slurry. This homogeneous slurry was subsequently spread onto a stainless-steel substrate. The amount of slurry applied, known as the mass loading, was carefully controlled to be approximately 0.7 mg/cm². Once spread, the electrodes were dried in an electric oven at 80 °C overnight, ensuring they were adequately prepared for the next phase of the supercapacitor fabrication. For the assembly of the supercapacitor, these DSAC electrodes were utilized as both the positive and negative electrodes. The gel electrolyte, which had been previously synthesized, was then integrated with these electrodes. The complete assembly was encapsulated within CR2032-type coin cells to finalize the supercapacitor's fabrication.

4.2.5 Characterization

The surface structure and morphology of the gel electrolyte were characterized using field emission scanning electron microscopy (FESEM, JOEL, JSM6610LV). The crystal structure was studied at room temperature using X-ray diffraction (XRD, Rigaku Miniflex-II diffractometer). The thermal properties of the gel electrolyte were investigated

using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). An SDR Q600 thermal analysis instrument was employed for the TGA analysis. An STA 449F3 thermal analysis instrument by NETZSCH was used for DSC analysis. Nanoindentation (Anton Paar STEP 500 Indentation Measurement System, Switzerland) was employed to investigate the mechanical strength of the gel electrolyte. All electrochemical characterizations are conducted using the CHI 760E electrochemical workstation and at least each measurement was repeated three times to ensure that we obtained accurate results.

4.3 Results and discussion

4.3.1 Structural and surface analysis of the gel electrolyte

The surface morphology of the two electrolytes was compared using FESEM. **Figures 17a** and **17b** depict the FESEM images of the PVA-Li₂SO₄ gel electrolyte. It is evident from the figures that the Li₂SO₄ particles display significant agglomeration within the polymer matrix. This observation suggests a poor interaction between the polymer and the salt. The uneven dispersion of Li₂SO₄ particles can be attributed to the adhesive properties of PVA [43]. Introducing an IL into the system alters the microstructure of the gel electrolyte. The IL functions as a plasticizer, enhancing the miscibility between the polymer and other components in the gel electrolyte. This effect may arise from the formation of multiple hydrogen bonds between PVA chains and the IL molecules [44]. The PVA-Li₂SO₄-IL gel electrolyte, as depicted in **Figures 17d** and **1e**, exhibits a more homogenous microstructure with less agglomeration and uniform pore distribution (highlighted by red dotted circles). The pore diameter and wall thickness were measured using ImageJ software, revealing that the average pore diameter is approximately 25 μm and the average wall thickness is around 8 μm . **Figure 17c** displays the EDS spectra of the PVA-Li₂SO₄ gel electrolyte, revealing its predominant carbon, oxygen, and sulfur composition. The primary constituent in the gel electrolyte is carbon, attributed to the presence of PVA. Sulfur is present due to the inclusion of Li₂SO₄, while oxygen is detected in both PVA and Li₂SO₄. Furthermore, in the EDS spectra of the PVA-Li₂SO₄-IL gel electrolyte shown in **Figure 17f**, fluorine is observed in addition to carbon, oxygen, and sulfur. Fluorine is attributed to incorporating the IL in the sample.

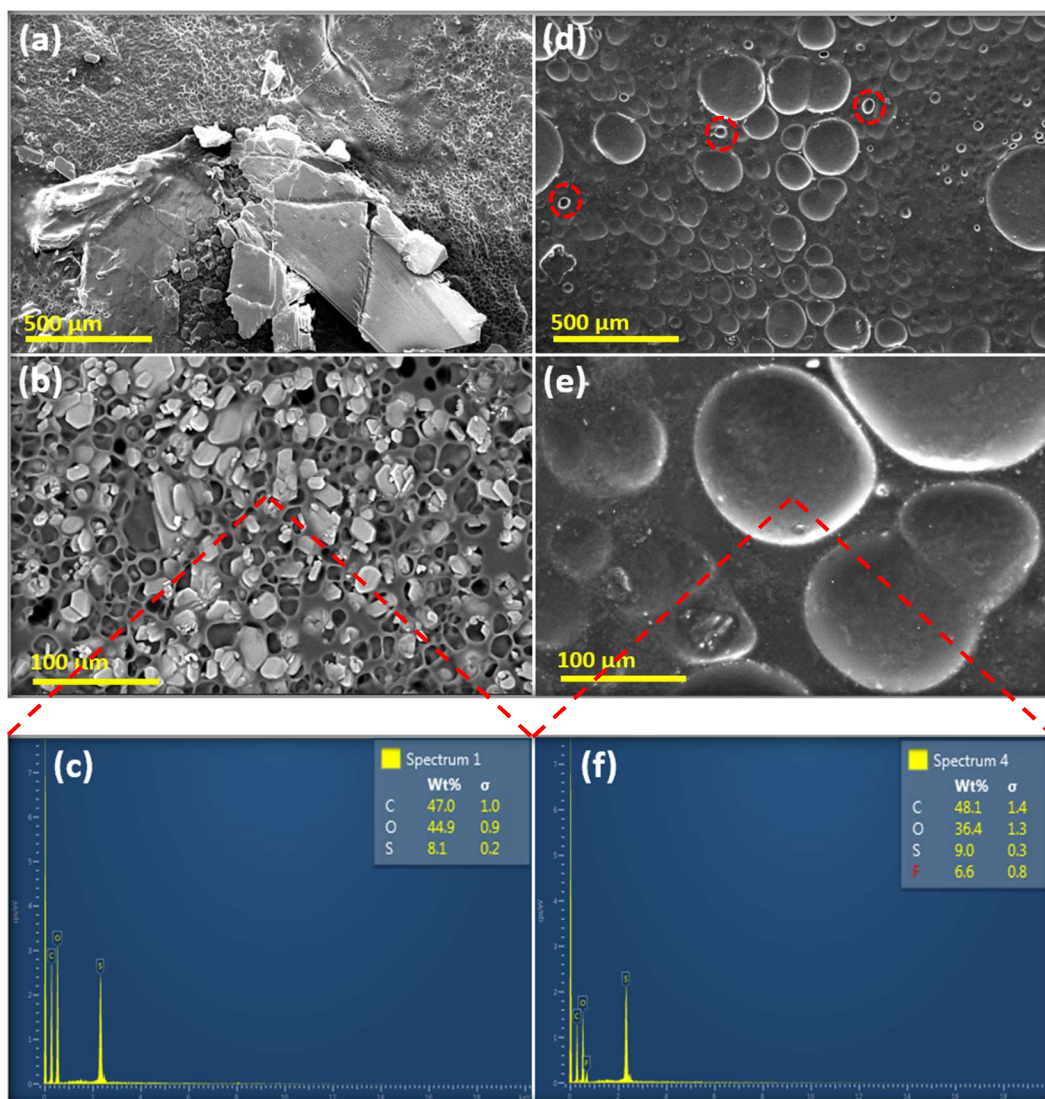


Figure 17. (a, b) FESEM micrographs of the PVA-Li₂SO₄ at different magnifications, and (c) its corresponding EDS spectrum. (d, e) FESEM micrographs of the PVA-Li₂SO₄-IL at different magnifications, and (f) its corresponding EDS spectrum.

To further investigate the physical role of IL in the gel electrolyte, elemental mapping using EDS was employed. As illustrated in **Figure 18a**, it is evident that carbon and oxygen display a uniform distribution throughout the surface of the PVA-Li₂SO₄ gel electrolyte. In contrast, sulfur exhibits agglomeration on one side. Conversely, in the case of the PVA-Li₂SO₄-IL gel electrolyte (**Figure 18b**), all constituent atoms are uniformly dispersed thanks to the plasticizing effect of the IL, thereby reaffirming the results obtained from the FESEM analysis.

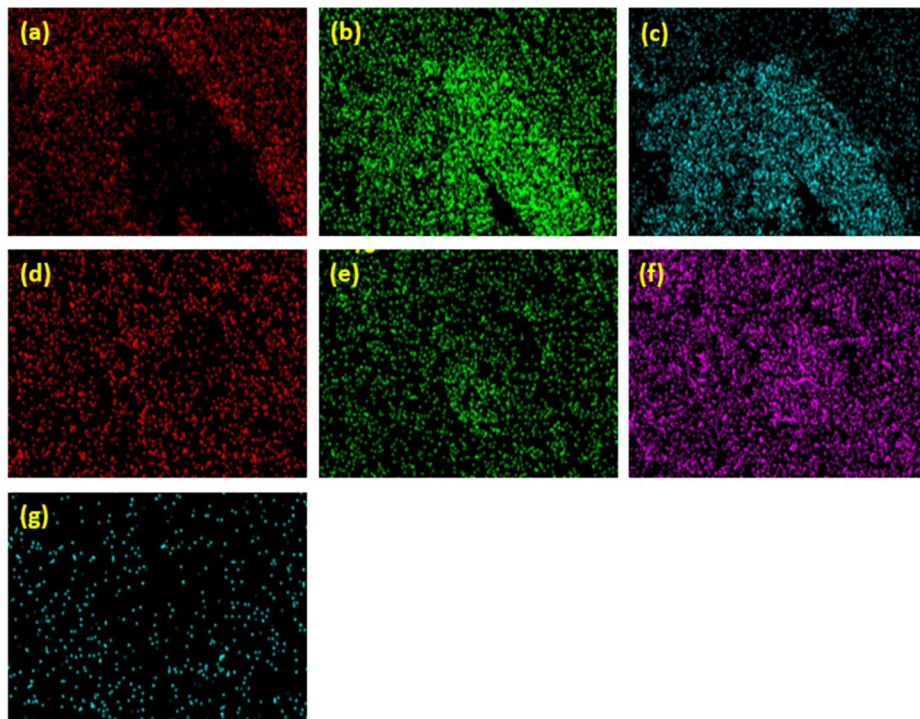


Figure 18. Elemental mapping showing the distribution of (a) C, (b) O, (c) S in PVA-Li₂SO₄ and (d) C, (e) O, (f) S and (g) F in PVA-Li₂SO₄-IL.

GPEs exhibit both crystalline and amorphous phases, which originate from the pure polymer's inherent crystalline/amorphous phases and the presence of the crystalline salt [45]. To probe the structural information of the developed gel electrolytes, XRD was employed. The XRD spectra of both electrolytes are shown in **Figure 19**. PVA-Li₂SO₄ displays prominent peaks in the low-angle region, around $2\theta \sim 17$, 24 , and 33 degrees, which are attributed to the presence of Li₂SO₄ in the gel electrolyte. These peaks correspond to the (001), (111), and (201) crystallographic planes of the Li₂SO₄ crystal lattice [46]. Interestingly, the XRD spectra of the PVA-Li₂SO₄-IL shows a slight shift in the position of the (001) and (111) planes to $2\theta \sim 14$, and 22.5 degrees, respectively, indicating an alteration in the microstructure of gel electrolyte. Therefore, not only does IL change the morphology of the gel electrolyte as concluded from FESEM data but cause some microstructural alteration as well. The XRD pattern of PVA often displays a broad hump or scattering continuum, typically in the range of $2\theta \sim 15 - 30$ degrees. This diffuse scattering arises from the amorphous arrangement of PVA chains, which lacks long-range periodicity [45].

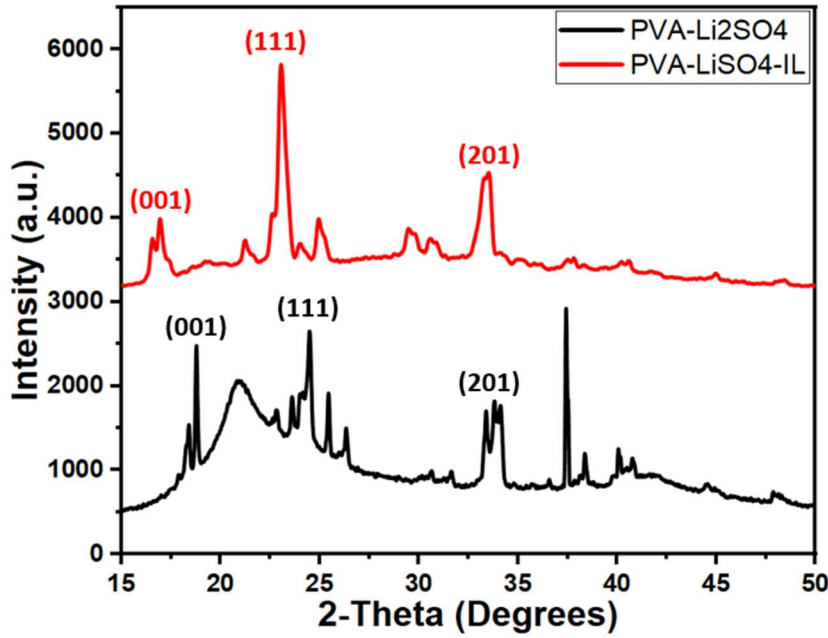


Figure 19: XRD spectra of the (a) PVA-Li₂SO₄ and (b) PVA-Li₂SO₄-IL gel electrolyte.

4.3.2 Ionic conductivity measurement

Ionic conductivity plays a crucial role in the performance of the gel electrolytes, in which high ionic conductivity is favored for energy storage devices. In addition, to ensure that the synthesized gel electrolyte functions in a wide range of temperatures, a 1 cm² gel electrolyte was pressed between two stainless steel spacers, coupled into a CR2032-type coin cell format, and subjected to EIS analysis to measure the ionic conductivity at different temperature settings. The EIS plots of the PVA-Li₂SO₄-IL gel electrolyte at different temperatures are shown in **Figure 20a**. **Figure 20b** shows the ionic conductivity curve of the PVA-Li₂SO₄-IL gel electrolyte measured at different temperatures. The ionic conductivity was calculated according to the equation ($\sigma_T = \frac{l}{R_b A}$), Where σ_T is the total ionic conductivity of the electrolyte, l is the thickness of the gel electrolyte, A is the contact surface area of the gel electrolyte, and R_b represents the electrolyte bulk resistance, which can be obtained from the intercept on the real axis of the Nyquist plot [50]. **Figure 20b** shows that the ionic conductivity increases as the temperature increases, attaining the highest value of 31.42 mS/cm² at 80 °C. The observed increase in ionic conductivity with rising temperature can be attributed to the following underlying mechanisms: at lower

temperatures, the mobility of ions and segmental motions of polymer chains are constrained due to strong associations between the salt and polymer. In contrast, at higher temperatures, the ionic conductivity increases due to a reduction in salt-polymer associations and an enhancement in the thermal segmental motion of polymer chains [48]. This results in quite a complex behavior; when the polymer is heated to a higher temperature (100 °C), there is a massive drop in the ionic conductivity of the electrolyte. This drop may be attributed to the polymer's glass transition, which occurs at approximately 96.62 °C. This transition is associated with the relaxation process of the glass transition (T_g) and arises from the micro-Brownian motion of the polymer chain backbone [49].

4.3.3 Linear sweep voltammetry (LSV)

Furthermore, a two-electrode system Linear Sweep Voltammetry (LSV) was conducted to determine the operating potential window (OPW) of the electrolyte. The OPW serves as a critical parameter for an electrolyte, delineating the maximum operational voltage limit for electrochemical energy storage devices such as batteries and supercapacitors [28]. Illustrated in **Figure 20c** is the LSV curve of the PVA-Li₂SO₄-IL conducted at a scan rate of 100 mV/s from -3 to 3 V. From the curve, the OPW was determined to be approximately 4 V (from -2 to +2), indicating the high stability of the electrolyte. This implies that our developed electrolyte remains free from decomposition at high potentials, addressing a significant drawback of aqueous-based electrolytes.

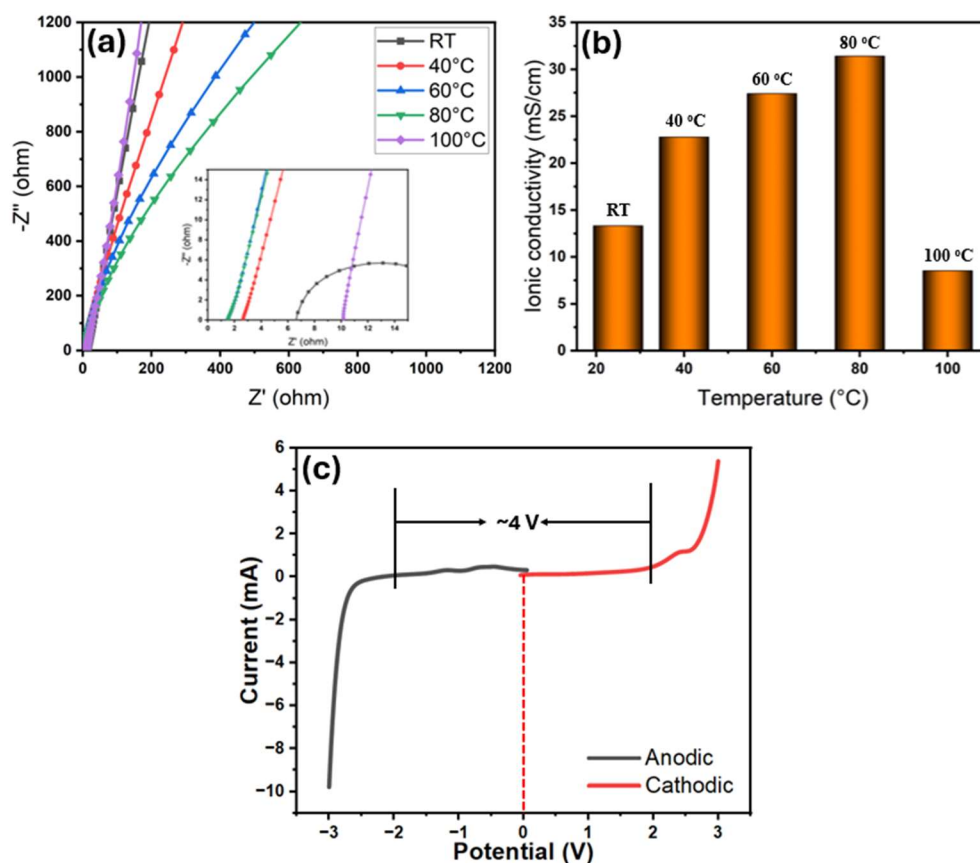


Figure 20. (a) The EIS Nyquist plots and (b) the ionic conductivity of the PVA-Li₂SO₄-IL gel electrolyte at different temperatures, (c) LSV spectra, indicating the stable OPW of the electrolyte (Potential versus Ag/AgCl).

4.3.4 Thermal stability and hardness

Anton Paar nanoindenter was used for the nanoindentation test. In this research, a Berkovich indenter was employed to analyze the gel electrolyte's deformation characteristics and mechanical properties. The experimental parameters are summarized in Table 6.

Table 6. Experimental parameters for nanoindentation test.

Indenter	Maximum load (mN)	Loading rate (mN/min)	Unloading rate (mN/min)	Holding time (s)
Berkovich	50	100	100	10

The samples were loaded at a constant displacement rate of 100 mN/min to ensure consistent measurements and avoid strain-hardening effects. In the case of PVA-Li₂SO₄, the load increment continued until the indenter reached a depth of ~19000 nm into the surface. Whereas, in PVA-Li₂SO₄-IL, the penetration is ~15000 nm, indicating improvement in the hardness of the material. To prevent significant creep that could impact the unloading behavior, the load was held at its maximum value of 50 mN for 10 seconds. Subsequently, the indenter was gradually withdrawn from the surface at the same rate until the maximum load reached a value of zero. The nanoindentation loading-unloading curve is shown in **Figure 21a**. The nanoindentation hardness and the elastic modulus of the gel electrolytes were calculated according to equations 1 and 2 [37,51], and their values are 2.7 MPa, 2 MPa and 0.057 GPa, 0.035 GPa, for PVA-Li₂SO₄-IL and PVA-Li₂SO₄ respectively.

$$H = \frac{P_{max}}{A_c} \quad (1)$$

$$E = \frac{E_i(1-V^2)}{\frac{2\beta\sqrt{A_c}E_i}{S\sqrt{x}}(1-V^2)} \quad (2)$$

$$S = \frac{dP}{dh} = 2\beta E_r \sqrt{\frac{A}{\pi}} \quad (3)$$

Where H is the hardness, P_{max} is the maximum load, and A_c is the contact area between the indenter and the specimen, E is the elastic modulus of the sample, E_i is the elastic modulus of the indenter, V is the poisons ratio of the sample, V_i is the poisons ratio of the indenter, β is a geometric constant of the indenter, and S is the stiffness which is the slope of the initial unloading curve and is given by the equation below. In this research, $V = 0.3$, $E_i = 1141$ GPa, and $V_i = 0.07$. $\beta = 1.034$ for the Berkovich indenter.

Figure 21b presents the results of TGA, which was employed to investigate the thermal stability of the gel electrolytes. The analysis was conducted between a temperature range of 25~800 °C and a heating rate of 10 °C/minute. The evaporation of water can be attributed to the weight loss observed in the gel electrolytes within the temperature range of 30 to 192 °C [50]. According to **Figure 21b**, the PVA-Li₂SO₄ gel electrolyte shows a significant degradation in the range of 200~300 °C and remains with reduced degradation

rate up to 500 °C. The PVA-Li₂SO₄-IL shows higher stability up to around 400 °C and then the degradation rate is accelerated. This further degradation observed when IL is introduced into the system is associated with the degradation temperature of the IL, which is around 400 °C [246], [247][54,55]. This analysis indicated that our synthesized gel electrolyte can be applied even at high temperatures up to 150 °C with minimal degradation compared to PVA-Li₂SO₄ gel electrolyte.

The DSC thermogram of the gel electrolytes is displayed in **Figure 21c**. From the graph, the melting temperature of the PVA-Li₂SO₄ was observed at ~216 °C, which has been increased to ~228 °C in case of PVA-Li₂SO₄-IL. This enhancement in melting temperature can be attributed to strong interaction between the PVA-Li₂SO₄ and IL. Although, the glass transition temperature (T_g) of pure PVA is ~96.2 °C [48], our PVA-Li₂SO₄ shows enhanced T_g at ~130 °C. This has further been enhanced to ~150 °C in case of PVA-Li₂SO₄-IL. Certain changes in the DSC thermograms of gel electrolytes such as enhancement in the melting and glass transition temperatures indicate the strength salt–polymer interaction [49].

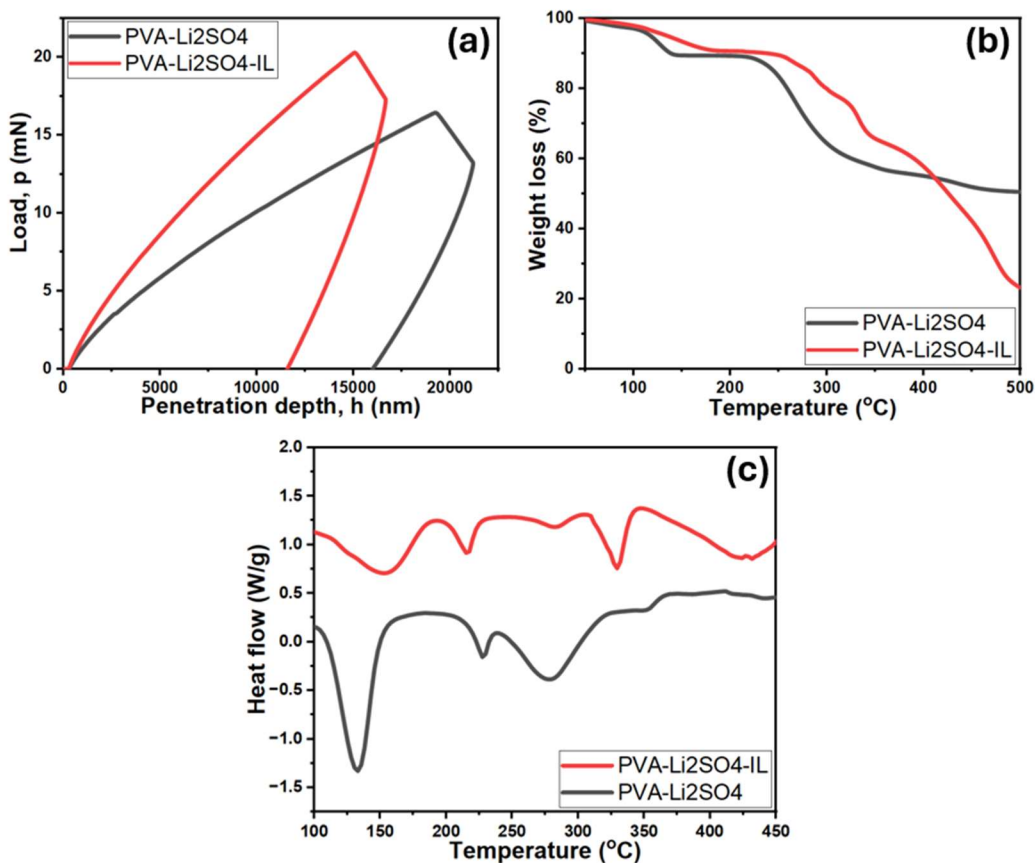
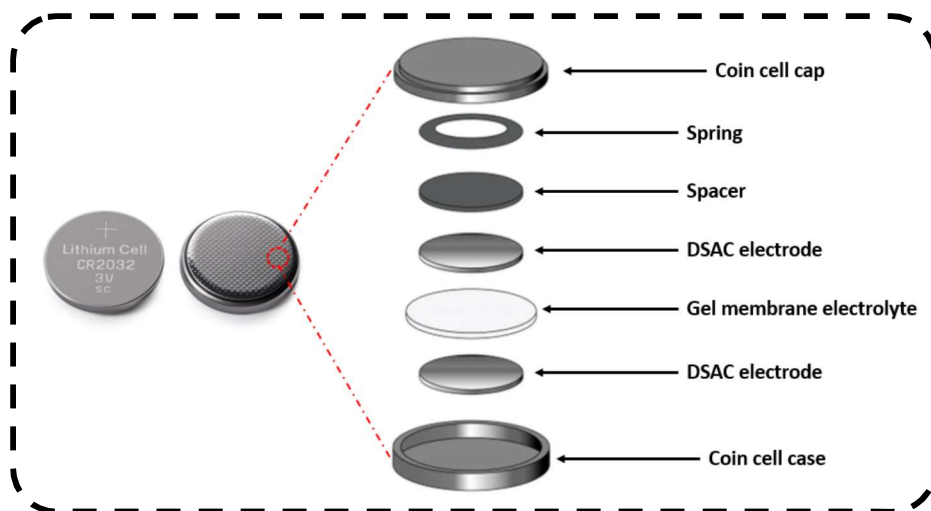


Figure 21. (a) Load-indentation depth curve, (b) TGA curve, and (c) DSC thermogram of the gel electrolytes.

4.3.5 Electrochemical performance

Two supercapacitor devices were assembled, each utilizing a different gel electrolyte: one with a PVA-Li₂SO₄ gel electrolyte and the other incorporating a PVA-Li₂SO₄-IL gel electrolyte. In both devices, the gel electrolytes served dual roles as both separators and electrolytes. The electrodes, made from DSAC coated on stainless-steel, functioned as both the positive and negative electrodes. To assemble the supercapacitor, the DSAC electrodes and the respective gel electrolyte were carefully placed into a CR2032-type coin cell casing. Once positioned, the assembly was securely crimped using an MSK-160E electric crimper, thus forming a symmetric supercapacitor device. The entire assembly process and the structure of the supercapacitor are clearly delineated in **Scheme 5** below.



Scheme 5. Schematic of the coin cell assembly for the symmetric supercapacitor fabrication using DSAC as electrode active materials and gel electrolyte as electrolyte and separator.

Before assessing the electrochemical performance of the fabricated supercapacitor device, its maximum OPW should be initially investigated. Initially, CV was conducted at different OPWs at a constant scan rate of 50 mV/s. **Figures 22a** and **22b** show the CV curves of the supercapacitor devices fabricated using PVA-Li₂SO₄ and PVA-Li₂SO₄-IL gel electrolyte electrolytes at different OPWs ranging from 0 to 2 V. As seen from the figures, the CV curves of both devices displayed quasi-rectangular shapes [233], [248], [249] without obvious water oxidation peaks up to 2 V. This value is far greater than the OPW of the aqueous electrolytes. Thus, the obtained gel electrolyte is suitable for high-energy-density applications. CV curves were also recorded at different scan rates ranging from 10 to 150 mV/s to assess the stability of the fabricated devices further. The CV curves of the fabricated devices at different scan rates and optimum OPW of 2 V are displayed in **Figures 22c** and **22d**. However, the CV curves of the PVA- Li₂SO₄-IL-based device show a pair of oxidation-reduction (redox) peaks due to the inclusion of IL. The appearance of redox peaks promotes pseudocapacitance, which is in addition to the EDLC. In our developed supercapacitor, the charge and discharge mechanisms involve complex interactions between the electrolyte components and the activated carbon electrodes. During charging, lithium ions (Li⁺) from Li₂SO₄ and anions from 1-butyl-3-methylimidazolium trifluoromethanesulfonate (IL) migrate towards the oppositely charged

electrodes. Li^+ ions adsorb onto the negative electrode [247], [250][55,56], forming an electric double layer, while IL anions adsorb at the positive electrode. The presence of IL enhances charge storage due to improved ion transport and adsorption [57]. During discharge, Li^+ ions and IL anions desorb from the electrodes and recombine in the electrolyte, allowing electron flow from positive to negative electrode, generating electric current. In addition, several other factors might be responsible for the observed redox peaks, and they may include the interaction between nitrogen functional groups found in the IL, $-\text{C}=\text{O}$ functional groups in the electrode materials, or $-\text{C}-\text{O}^-$ functional groups present in the PVA with Li^+ ions in the salt or even interaction between impurities. N/O-rich functional groups in the system can cause reversible pseudocapacitance represented by a pair of redox peaks observed in the CV spectra. Plausible mechanisms for the observed redox reaction are given in equations 5 to 7 below [54].



$$C_s = \frac{\int I \times \Delta V}{m \times v \times \Delta V} \quad (7)$$

From the CV curves in **Figures 22a** and **22b**, the specific capacitances at different OPWs were calculated based on the area under the curve for both devices, using equation (7). The expression $\int I \times \Delta V$ represents the area under the CV curve, measured in watts. In this context, m denotes the average mass of the active material present on both electrodes, expressed in grams. The symbol v refers to the scan rate, which is quantified in volts per second (V/s). Lastly, ΔV stands for the OPW, and it is measured in volts. The specific capacitance at different OPWs of 1, 1.2, 1.4, 1.6, 1.8, and 2 V were respectively found to be 33, 34.4, 35.4, 37.5, 39.1, and 43.1 F/g for the PVA- Li_2SO_4 -based symmetric supercapacitor. Similarly, for the PVA- Li_2SO_4 -IL-based symmetric supercapacitor, the values of the specific capacitance are 70, 71.4, 72.4, 74.1, 77.6, and 82.6 F/g at various OPWs of 1, 1.2, 1.4, 1.6, 1.8, and 2 V, respectively. Moreover, the specific capacitances at different scan rates were also evaluated from the CV curves (**Figures 22c** and **22d**) of both

devices. The specific capacitances according to the CV curves were found to be 112.69, 98.17, 82.48, 75.19, 71.6, and 64.91 at the scan rates of 10, 20, 50, 80, 100, and 150 mV/s, respectively, for the PVA-Li₂SO₄-IL-based supercapacitor. Similarly, the specific capacitance of the PVA-Li₂SO₄-based device was calculated from the CV and was found to be 58.55, 49.6, 43.13, 34.54, 30.99 and 29.38 at 10, 20, 50, 80, 100 and 150 mV/s, respectively.

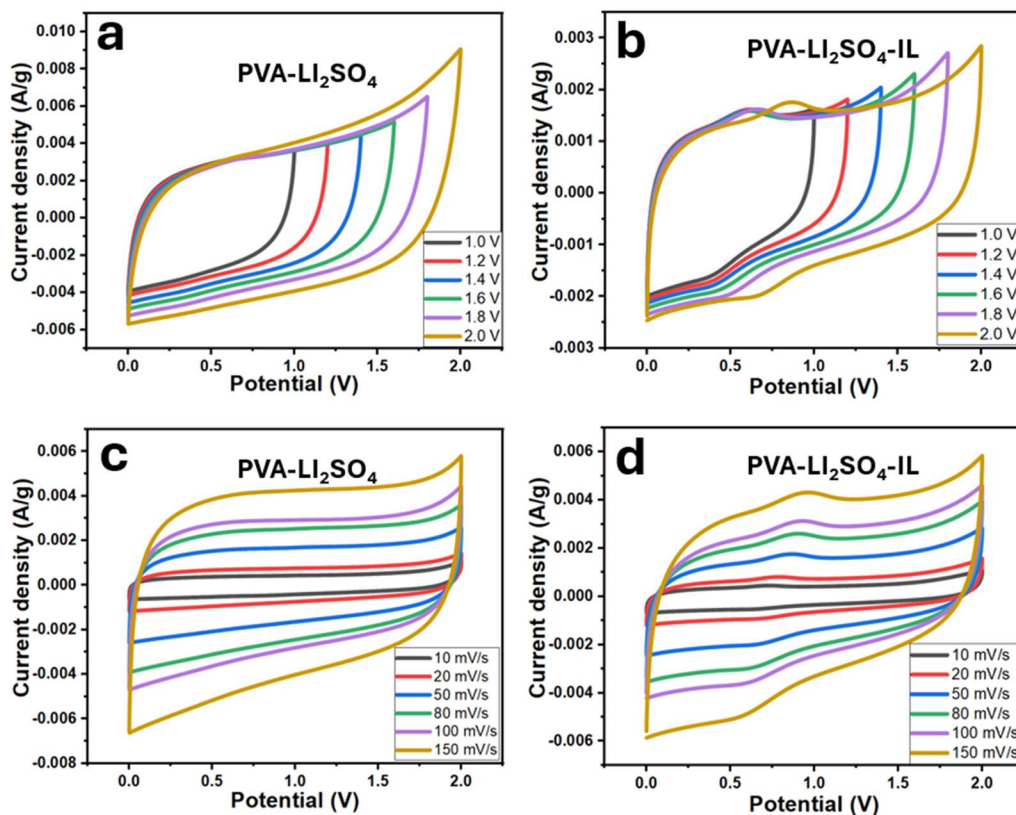


Figure 22: CV curves of (a) PVA-Li₂SO₄ and (b) PVA-Li₂SO₄-IL based symmetric supercapacitors at different OPWs and constant scan rate of 50 mV/s. CV curves of (c) PVA-Li₂SO₄ and (d) PVA-Li₂SO₄-IL based symmetric supercapacitors at various scan rates.

GCD at different OPWs and constant current densities were investigated further to evaluate the electrochemical performance of the fabricated supercapacitors. The GCD cycles of both devices were stable up to 2 V, which is displayed in **Figures 23a** and **23b**. **Figure 23c** and **23d** represent the GCD curves of the PVA-Li₂SO₄ and PVA-Li₂SO₄-IL based supercapacitors, respectively, at different current densities. The GCD curves

exhibited almost symmetric triangular shapes without apparent IR drops, indicating a rapid charge-discharge process and a typical EDLC behavior. Both devices show robust performance. In the developed symmetric supercapacitors, redox peaks observed in CV but absent in GCD highlight the distinct electrochemical behaviors captured by these techniques. CV, with its potential sweep, is sensitive to faradaic processes like redox reactions, evident in the observed peaks. In contrast, GCD, operating under constant current, emphasizes capacitive (non-faradaic) mechanisms, evident in the triangular GCD curves, indicative of charge storage through electrostatic accumulation rather than redox reactions. This difference underscores the varying responses of electrode materials and electrolytes under different testing conditions. The specific capacitance, energy, and power of the fabricated devices were calculated from the GCD results using the equations (8-10) [63].

$$C(\text{F/g}) = \frac{I \times \Delta t}{m \times \Delta V} \quad (8)$$

$$E(\text{Wh/kg}) = \frac{1}{2} \frac{C \times \Delta V^2}{3.6} \quad (9)$$

$$P(\text{W/kg}) = \frac{E \times 3600}{t} \quad (10)$$

Where, I is the applied current, Δt is the discharge time, m is the mass of the active material on both electrodes, ΔV is the operating voltage window, C is the specific capacitance, E is the energy density, and P is the power density.

The specific capacitance was calculated from the device's discharge time and the electrode material's total active mass using Equation 9. We calculated the specific capacitance at different OPWs and constant current density of 5 A/g for both devices using the data in **Figures 23a** and **23b**. From the data, the specific capacitance for the PVA-Li₂SO₄-based device was found to be 27.55, 27.63, 27.75, 28.98, 31.08, and 33.29 F/g at the OPWs of 1, 1.2, 1.4, 1.6, 1.8, and 2 V, respectively. Similarly, the specific capacitance of the PVA-Li₂SO₄-IL-based supercapacitor at the OPWs of 1, 1.2, 1.4, 1.6, 1.8, and 2 V was found to be 36.08, 39.09, 41.39, 44.49, 48.01, and 57.5 F/g, respectively. Furthermore, we evaluated the specific capacitance at different current densities for both devices from the GCD spectra in **Figures 23c** and **23d**. According to the data, the PVA-Li₂SO₄-based

device shows a maximum specific capacitance of 56.75 F/g at 0.5 A/g and 30 F/g at a high current density of 5 A/g. Interestingly, introducing IL into the PVA-Li₂SO₄ system imposes some pseudo capacitance and dramatically increases the capacitive properties of the device. The specific capacitance was calculated from the GCD profile of the PVA-Li₂SO₄-IL-based supercapacitor. It was found to be as high as 117.25 at 0.5 A/g (about 210% of the capacitance of a pure PVA-Li₂SO₄-based device) and remains high at high current density, with a value of 57.5 F/g at 5 A/g.

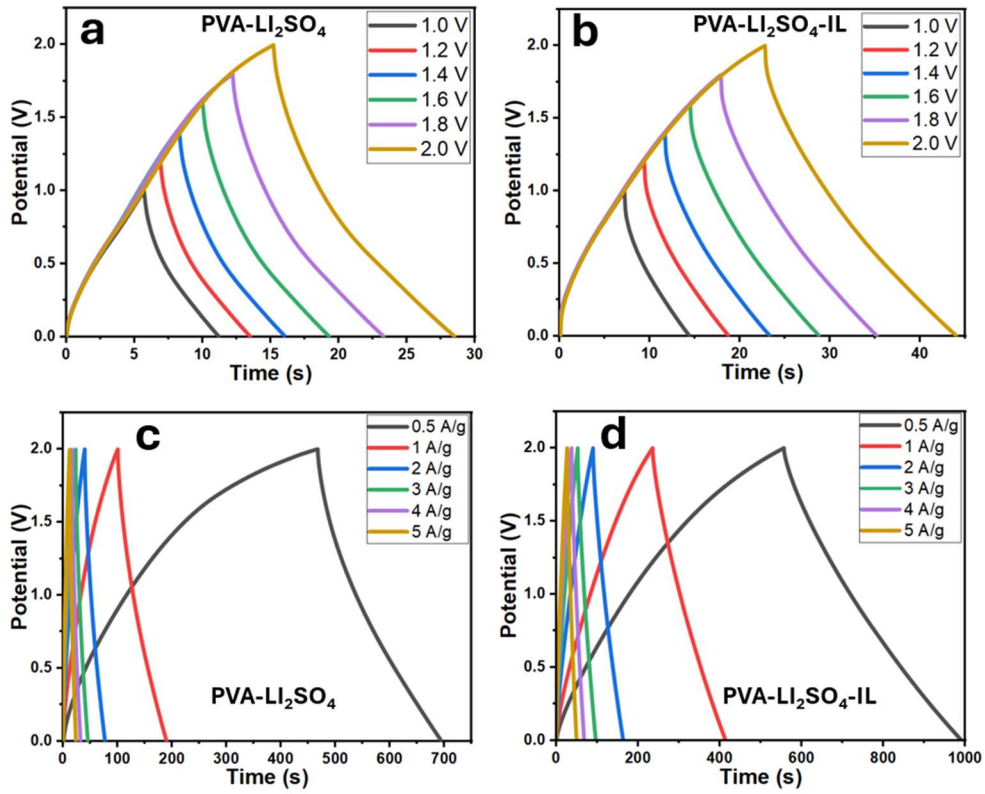


Figure 23: GCD curves of (a) PVA-Li₂SO₄ and (b) PVA-Li₂SO₄-IL based supercapacitors at different OPW ranges at same current density of 5A/g. and GCD curves of (c) PVA-Li₂SO₄ and (d) PVA-Li₂SO₄-IL based supercapacitors at various current densities.

To gain an understanding of the electrochemical interface properties of the supercapacitor devices, EIS was utilized. **Figure 24a** compares the Nyquist plot of the PVA-Li₂SO₄ and PVA-Li₂SO₄-IL based symmetric supercapacitor devices. The bulk resistance of the supercapacitor, which comprises the electrolyte resistance and internal

electrode resistance, is represented by the intercept point on the real axis at the high-frequency region. Additionally, the charge transfer resistance can be determined by the diameter of the compressed semicircle [64]. By analyzing **Figure 24a**, it is evident that including an IL slightly reduces the bulk resistance from 6 to 4.9 ohms, as indicated by the intercept on the real axis of the Nyquist plot. **Figure 24b** depicts the Nyquist plot for the PVA-Li₂SO₄-IL based device before and after 1000 cycles. The story clearly illustrates a slight increase in resistance (from 4.9 to 6.8 ohms) after prolonged cycling at high current density. This increase can be attributed to the degradation of the electrolyte caused by the high current applied during the stability test. However, it should be noted that this degradation is negligible. Additionally, from **Figure 24b**, it is evident that incorporating an IL into the PVA-Li₂SO₄ system significantly enhances the efficiency of the fabricated device, even after extended cycling.

Energy density and power density are two critical parameters of supercapacitors that would limit their application. As shown in **Figure 24c**, both the energy density and the power density decrease with the increase of current density, which is a common trend for supercapacitors. According to equations (9) and (10), the maximum energy density attained by the PVA-Li₂SO₄-IL-based device is 65.15 Wh/kg at 500 W/kg. The PVA-Li₂SO₄-based device achieves an energy density of 31.5 Wh/kg under the same conditions. **Figure 24d** shows the evaluation of the cycling stability of the PVA-Li₂SO₄-IL-based supercapacitor under a current load of 10 A/g for 10000 GCD cycles. The results demonstrate that promising cycle stability is achieved even at a current load of 10 A/g. After 10000 GCD cycles, the capacitance retention was 88.7%. The fact that the Coulombic efficiency is close to 100% suggests high cycling stability and a high degree of charge-discharge reversibility. **Table 7** shows the electrochemical performance comparison of the developed symmetric supercapacitor with previously reported similar supercapacitors in the literature.

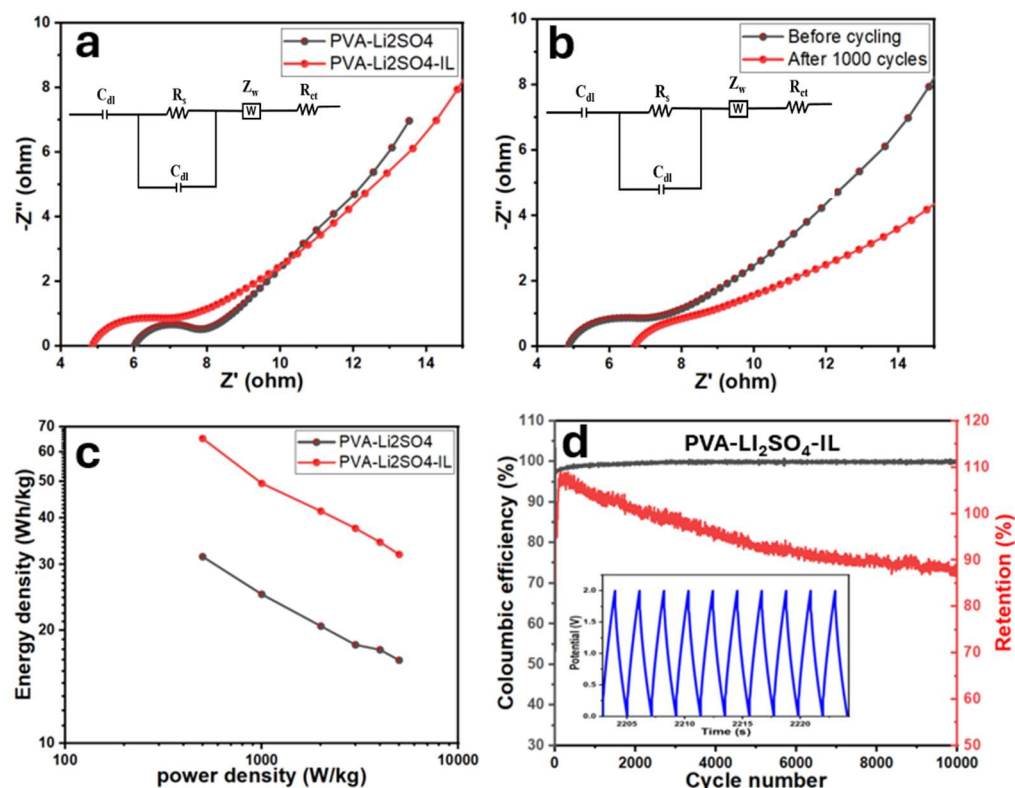


Figure 24. (a) Nyquist plots comparing the EIS response between PVA-Li₂SO₄ and PVA-Li₂SO₄-IL based symmetric supercapacitor devices. (b) EIS Nyquist plots of PVA-Li₂SO₄-IL-based device before and after 1000 GCD cycles (insert is the equivalent circuit model). (c) Ragone plots of the PVA-Li₂SO₄ and PVA-Li₂SO₄-IL based devices. (d) Cycling performance of the PVA-Li₂SO₄-IL-based supercapacitor at 10 A/g (the inset shows the last 10 cycles).

Table 7. Comparison of the electrochemical performance of the developed symmetric supercapacitor device with previously reported literature.

Electrolyte	OPW (V)	Ionic conductivity (mS/cm)	Energy density (Wh/kg)	Power density (W/kg)	Stability (%/cycles)	Ref.
PVA- H ₃ PO ₄ - [EMIM]BF ₄	1.2	39.3	54.3	23880	96/3000	[65]
PVA- Li ₂ SO ₄ BMIMI	1.5	46	29.3	...	80.9/10000	[42]

PVA- LiBr- [BMIM]Cl	1.6	15.2	16.3	932.6	93.4/10000	[67]
PVA-H₂SO₄- ARS	1.6	33.3	39.4	400	78/1000	[68]
PVA-NaCl	0.6	...	6.33	600	87/8000	[69]
PVA- Na₂SO₄- Pyr₁₄Br	2.0	27.1	33	459.2	81/8000	[70]
PVA-H₂SO₄- KI-VOSO₄	1.6	...	25.4	190	93.7/1000	[71]
PVA-Li₂SO₄- EMIMBr- CNT	1.8	61.1	43.1	220.9	87.9/10000	[72]
PVA- HMIMCl- KOH	1.6	2.82	22	1080	70.4/5000	[74]
PVA/BMIMC I/Li₂SO₄	1.5	37	10.6	...	90/3000	[64]
PVA-H₂SO₄- AQQS	1.0	28.5	30.5	350	91/1000	[75]
PVA/Na₂SO₄	2.0	...	0.92 mWh/cm ³	28.6 mW/ cm ³	85/4000	[76]
PVA-LiCl	1.8	...	184.5 μWh/cm ²	0.92 mW/cm ²	90/10000	[78]
PVA-KOH- KI	1.6	13.21	41.308	464.72	89.3/5000	[79]
PVA-KOH- KI	1.0	12.73	7.8	15340	95.76/1000	[15]
PVA-LiClO₄	1.8	...	11.63	4890	85.5/4000	[80]
PVA-Li₂SO₄- IL	2.0	31.42	65.14	5000	83.3/1000	This work

4.4 Conclusion

In this research, we have successfully developed a high-energy-density supercapacitor, leveraging the unique properties of a PVA-Li₂SO₄-IL gel electrolyte in conjunction with DSAC electrodes. This electrolyte, synthesized through a solution casting method, demonstrated high ionic conductivity, reaching a peak value of 31.42 mS/cm at 80 °C. The symmetric supercapacitor, constructed using this novel electrolyte, achieved significant performance metrics compared to bare PVA-Li₂SO₄, including an energy density of 65.14 Wh/kg at 500 W/kg. Additionally, the assembled supercapacitor using PVA-Li₂SO₄-IL exhibited high cycling stability, maintaining 88.7% capacitance retention and approximately 100% coulombic efficiency even after 10000 cycles. These results not only underscore the efficacy of the PVA-Li₂SO₄-IL gel electrolyte in enhancing the electrochemical performance of energy storage devices but also open avenues for its application across various other electrochemical fields. Looking ahead, the potential of ionic liquid usage in the gel electrolyte development could lead to the development of next-generation safe and high energy density energy storage systems.

CHAPTER 5

All-biomass Supercapacitors with Date Stone-Derived Activated Carbon Electrodes and Cellulose Hydrogel Electrolyte

Abstract

Date stone biomass is one of the major agricultural byproducts in Saudi Arabia. Without a proper disposal system, they constitute waste that litters the environment. In this research, we for the first time propose an all biomass supercapacitor based on date stone biomass. The supercapacitor features date stone-derived activated carbon (DSAC) as electrodes and date stone derived cellulose hydrogel (DSDC-NaOH-Urea) as electrolyte. The electrochemical performance evaluation of the supercapacitor revealed remarkable performance with excellent cycle stability of 107.42% capacitance retention and 100% columbic efficiency after 5000 cycles. Additionally, the supercapacitor exhibits a high specific capacitance of 113.75 F/g at 0.5 A/g, high energy density of 40.44 Wh/kg at 400 W/kg, which remain as high as 20 Wh/kg at high power density of 4000 W/kg. Moreover, the supercapacitor attains a wide OPW of 1.8 V which is by far greater than the OPW of conventional aqueous electrolytes. This research demonstrated the potential of using local resources such as date stone biomass, to produce a cheaper and environmentally benign electrochemical energy storage devices. In addition, the research do not only aid in waste management, but also serve as an economical platform for sustainable energy production technologies.

5.1 Introduction

The world must drastically reduce its dependency on fossil fuels to meet the growing energy demand worldwide and protect the environment. Central to this endeavor is the capability to effectively convert, store, transport, and access energy using renewable sources. Hence, energy storage devices derived from biomass will play a crucial role in the upcoming years due to the escalating environmental challenges [258]. Interestingly, in the

recent years, numerous kinds of biomass have been employed for the development of carbonaceous electrodes for supercapacitors. For example, A D Shuaibu et al. employed date stone biomass to develop activated carbon with high surface area ($1612 \text{ m}^2/\text{g}$) which was later employed to construct a symmetric supercapacitors with high performance [259]. Numerous other biomass have been reported in the literature for the fabrication of carbonaceous electrodes and they include cherry stones [40], date leaves [42], jute sticks [43], [44], [45], leaves of tal palm [46], *Syzygium cummini* leaves [47], *Albizia procera* leaves [48], waste of tea leaves plants [49], and microorganisms [50].

Besides the electrode, the separator is another important component of the supercapacitor. Unfortunately, the conventional supercapacitor separators are usually obtained from petrochemical-based polymers such as poly(ethylene oxide) (PEO), poly(vinyl alcohol) (PVA), poly(methyl methacrylate) (PMMA), poly(acrylonitrile) (PAN), poly(vinylidene fluoride) (PVDF), and copolymer poly(vinylidene fluoride-hexafluoro propylene) (PVDF-HFP) [69], [127], [132]. Few studies exist on the use of biomass-derived polymers for the development of supercapacitor separators [260]. However, certain cellulose-based polymers, including hydroxyethyl cellulose, starch mixed with glycerol, and nano-fibrillated cellulose, have been utilized as separators in lithium-ion batteries. This indicates the potential usefulness of these biomaterials in other energy storage devices such as supercapacitors [258].

Dates (*Phoenix dactylifera L.*), cultivated in tropical regions as a flowering plant belonging to the palm family *Aceraceae*, are renowned for their sweet and edible fruits. The date palm exhibits a remarkable structural organization, high lignocellulosic nature, and low ash content. The composition of date palm includes 42% cellulose, 18% hemicellulose, 25% sugar and other compounds, 11% lignin, and 4% ash [259]. The Date seeds account for 11–18% of the weight of the date fruit [60] which can be utilized to create innovative sustainable bioproducts, such as activated carbon [59] and cellulose [261]. This approach not only provides significant economic and environmental advantages but also yields a high-value biomaterial characterized by exceptional physical and chemical properties. According to a report from the United Nations' Food and Agriculture Organization, the annual production of dates in 2018 reached around 8.7 million tons, with

the majority of the products coming from the Middle East and North Africa region with Kingdom of Saudi Arabia (KSA) producing 0.9 million tons (which is about 10% of the global date production) [262], [263].

In this research, from the sustainability point of view and for the first time, we capitalized on naturally abundant date stone biomass to develop an all-date stone supercapacitors by utilizing date stone-derived activated carbon (DSAC) as electrodes and a hydrogel electrolyte (DSDC-NaOH-Urea) made of cellulose extracted from date stone. The supercapacitor exhibits remarkable electrochemical performance featuring high specific capacitance of 113.75 F/g at 0.5 A/g, high energy density of 40.44 Wh/kg at 400 W/kg, which remain as high as 20 Wh/kg at high power density of 4000 W/kg, and expanded OPW of 1.8 V. Additionally, the supercapacitor showed excellent cycling stability of 107.42% and ~100% columbic efficiency after 5000 cycles. This research showcase the potential of date stone in the development of high performance supercapacitors and provides an avenue for further research efforts in this direction especially in the middle east region where they have abundance of date stone biomass.

5.2 Materials and methods

5.2.1 Materials

We get date stone biomass from a local date stone plantation in Dhahran city, KSA. Sodium bicarbonate, sodium hydroxide, hydrochloric acid, sodium sulfite, nitric acid, potassium nitrate, toluene, ethanol, epichlorohydrin (ECH), and acetic acid were obtained from Sigma-Aldrich. Clorox bleach was purchased from a provision store at Khobar, Dhahran, KSA. Deionized water (18 M Ω resistance) was used for reagent preparation, while N-methylpyrrolidone (NMP), Polyvinylidene fluoride (PVDF), carbon black, and graphite foils were purchased from MTI corporation. Nitrogen gas of high purity was used for the synthesis of the activated carbon.

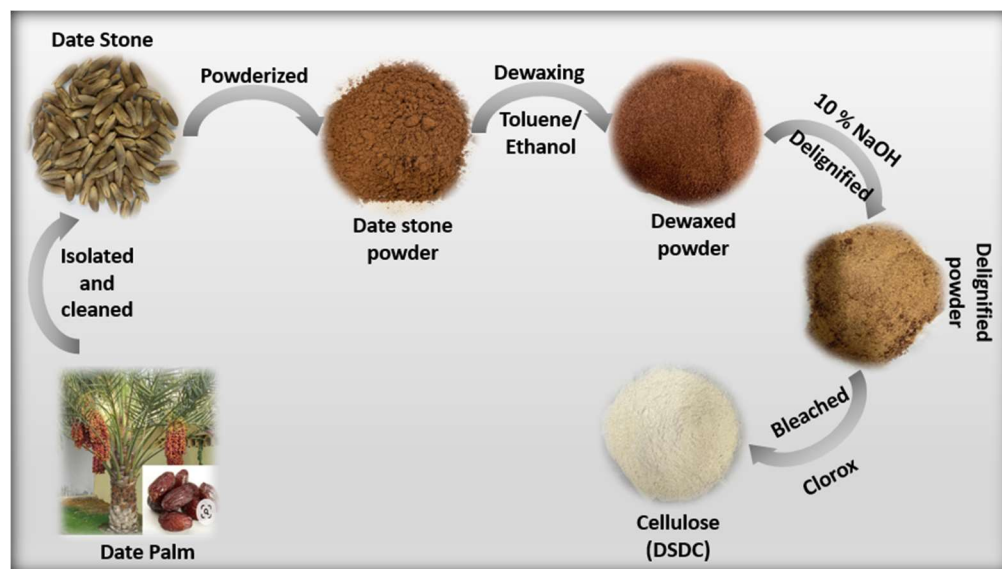
5.2.2 Synthesis of Activated Carbon (DSAC) from date stone

The date stone was first thoroughly cleaned with distilled water and dried in an air oven at 110 °C. The dried date stones were pulverized with a kitchen blender to obtain a fine powder and then passed through 300 micrometer mesh to obtain even more fine

powder. The activation process involves mixing the date stone powder with sodium bicarbonate in a one is to four ratio and subsequent heating to 750 °C in a tube furnace for eight hours under continuous flow of nitrogen gas. Afterwards, the obtained carbon was washed several times with 0.5 M HCl to neutralize the sodium bicarbonate and then with deionized water until the pH is approximately 7. The activated carbon is referred to as DSAC in the subsequent parts of the manuscript.

5.2.3 Cellulose Extraction from date stone

For the cellulose extraction, we followed the procedure described in [264] with few modification. Initially, 50 g of the date stone powder was dewaxed in a mixture of toluene and ethanol (2:1 ratio) for 6 hours at 60 °C under constant stirring at 500 rpm. After dewaxing, the mixture was decanted to separate the residue from the soluble components. The residue was then washed several times with ethanol and dried overnight in the open air. The obtained dried powder was then subjected to alkaline extraction using 10% (w/v) NaOH at 55 °C for 1.5 hours. The powder to NaOH ratio used was 1:10. After the extraction time elapsed, the mixture was filtered, and the residue was neutralized using 10 % (v/v) acetic acid and dried at 80 °C for 5 hours. The powder was delignified using a mixture of potassium nitrate and nitric acid (4 mg KNO₃ in 400 mL 3.5% HNO₃) at 90 °C for two hours under continuous stirring and then digested for 1 hour at 50 °C in 2% (w/v) NaOH and Na₂SO₃. The precipitate was filtered and washed with deionized water and then bleached Clorox bleach at 90 °C for 30 minutes before washing several times with deionized water till neutral pH and dried at 80 °C for 24 hours to obtain the cellulose. The Clorox bleach was used directly as purchased without any dilution. The complete extraction procedure is summarized schematically in the figure below. The obtained cellulose was denoted as date stone-derived cellulose (DSDC) in subsequent parts of the manuscript.



Scheme 6. Cellulose extraction procedure.

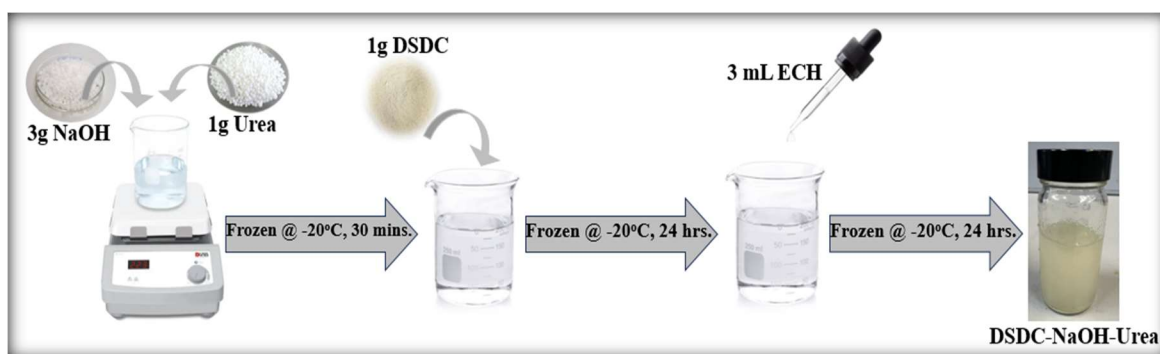
5.2.4 Characterization

To characterize the cellulose, first XRD was employed to study the crystallinity of the sample. A Rigaku MiniFlex X-ray diffractometer coupled with Cu-K α radiation operating at 40 kV and 15 mA at room temperature was employed. Furthermore, FT-IR was used to identify surface functionalities of the cellulose. NICOLET 6700 FT-IR spectrometer (by Thermo scientific) was used for the analysis. Field emission SEM was employed to study the surface morphology of the DSAC. A Thermo scientific Quattro S field emission scanning electron microscope coupled with EDX detector was used for the SEM analysis. All electrochemical characterizations are conducted using the CHI 760E electrochemical workstation and at least each measurement was repeated three times to ensure that we obtained accurate results.

5.2.5 Preparation of DSDC Hydrogel Electrolyte (DSDC-NaOH-Urea)

Initially, 40 mL aqueous solution containing 3.0 g NaOH and 1g Urea was precooled at -20 °C for 30 minutes. Then 1.0 g of DSDC was added to the above solution and stirred for 5 minutes to disperse the cellulose before stored at -20 °C for 24 hours. The resultant frozen solution was then thawed at room temperature and stirred to obtain a transparent solution. Subsequently, 3 mL of epichlorohydrin was added to the solution and stored at -20 °C for another 24 hours to allow cross linking to take place. Afterwards, the

resultant solution was thawed at room temperature and agitated at 2000 rpm in a thinky mixer to remove air bubbles and to obtain a highly viscous cellulose hydrogel. The hydrogel is henceforth referred to as date stone-derived cellulose hydrogel electrolyte (DSDC-NaOH-Urea). The schematic illustration of the DSDC hydrogel is summarized in **Scheme 7**.



Scheme 7. Schematic illustration of the DSDC hydrogel preparation.

5.3 Results and discussion

5.3.1 Structural and surface analysis of the Cellulose (DSDC)

Figure 25a shows the XRD spectra of the date stone-derived cellulose (DSDC). Cellulose comprises of both crystalline and amorphous phases. The sharp peak at 2-theta ~ 16.1 , 22.5 , and 34.5 are associated with 110, 200, and 004 crystal planes respectively of a typical cellulose I polymorph [262], [265]. The occurrences of these peaks established that the crystalline structure of cellulose I was still conserved after the alkaline-assisted extraction of cellulose nanocrystals from raw date stones [266]. The FT-IR spectra of the cellulose isolated from date stones (DSDC) is shown in **Figure 25b**. The wide absorption band detected within the range of 3400 to 3500 cm^{-1} corresponds to the stretching vibration of the inter-hydrogen bonded OH group, while the band around 2900 cm^{-1} signifies the presence of CH groups in cellulose [261], [262], [267]. The prominent peak at approximately 1049 cm^{-1} is associated with the stretching vibration of C-O-C in the pyranose skeletal ring [268]. Cellulose exhibits hydrophilic properties, leading to strong interactions with water at a molecular level, as indicated by the absorption peak around 1645 cm^{-1} , which is attributed to OH bending in water [261], [267]. Additionally, the bands

observed around 1610 and 1344 cm^{-1} in the leaflet and fiber cellulose samples are assigned to CH_2 stretching of an aromatic ring and C–O stretching of an ether linkage, respectively. The absorption bands at approximately 1735 cm^{-1} are attributed to C=O, potentially originating from a ketone within the hemicellulose residue or resulting from partial acetylation of cellulose during the bleaching process, as reported previously [267], [269].

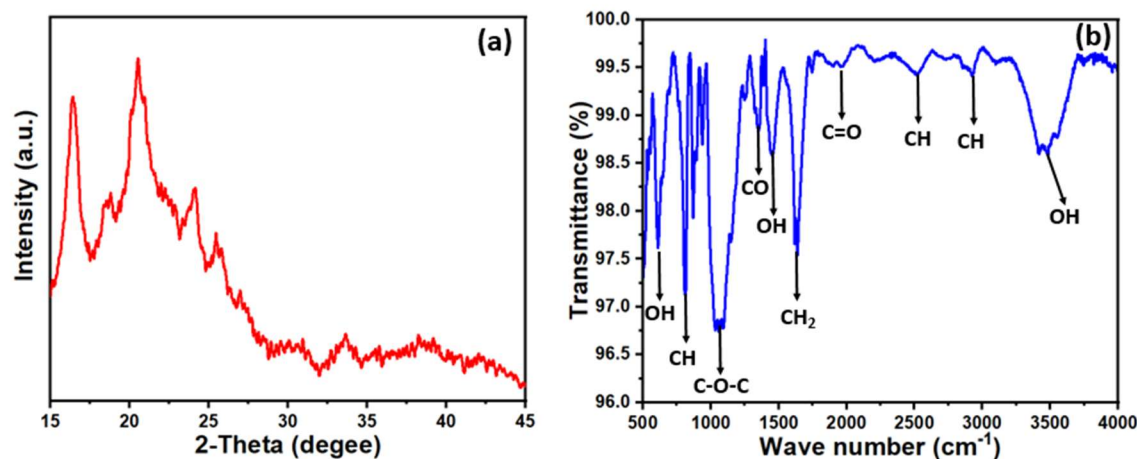


Figure 25. (a) XRD spectra, (b) FT-IR spectra of the DSDC.

The surface morphology of the DSDC was analyzed using field emission scanning electron microscopy (FESEM). The FESEM spectra of the DSDC shown in **Figure 26a and b** exhibit a sheet type morphology. The surface is rough, irregular, and porous, thus able to provide a large surface area that is favorable for ionic conduction as well as physical and chemical interactions. The EDS analysis (as depicted in **Figure 26c**) revealed that the DSDC has a predominant composition of carbon and oxygen, with trace amount of sodium.

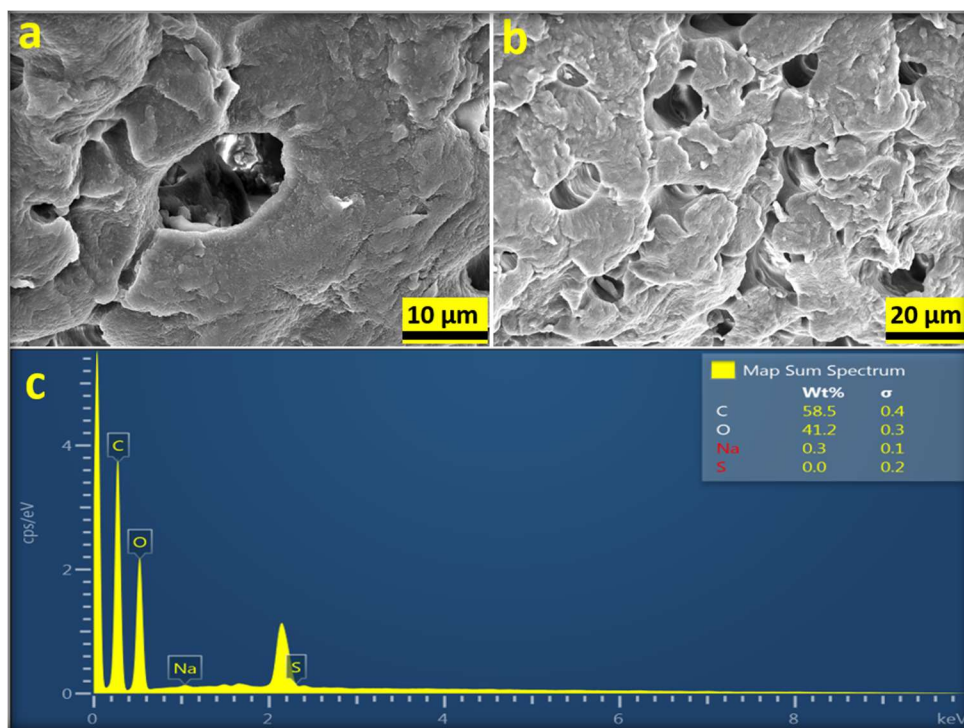
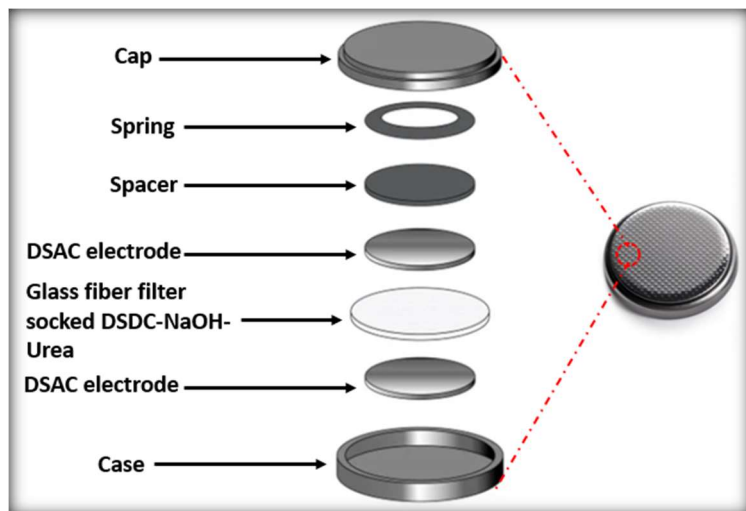


Figure 26. (a and b) SEM spectra at different magnification, (c) EDS spectra of the DSDC.

5.3.2 Fabrication of the supercapacitor

To assemble the supercapacitor, glass fiber filter soaked in DSDC-NaOH-Urea was sandwiched between two DSAC electrodes and packed in a CR 2032 coin cell and carefully crimped using an electric crimper, thus forming the symmetric supercapacitor. The DSAC electrode was prepared by mixing DSAC, conductive carbon, and PVDF binder in a 7.5:1.5:1 ratio. NMP solvent was added to create a slurry. The slurry was subsequently spread onto a graphite foil substrate and dried at 80 °C overnight. After drying, the mass loading was found to be approximately 0.7 mg/cm². The fabrication process and the entire coin cell assembly is summarized in the **Scheme** below.



Scheme 8. Schematic illustration of the coin cell supercapacitor.

5.4 Electrochemical Performance

5.4.1 Ionic conductivity measurement

The ionic conductivity is very important for energy storage devices. Ionic conductivity is determined by the number of charge carriers in the electrolyte and the ease of mobility of those charge carriers. Therefore, we measured the ionic conductivity of the hydrogel electrolyte at different temperatures. EIS was employed to measure the resistance of the electrolyte in two electrode systems. The ionic conductivity was calculated using the equation ($\sigma_T = \frac{l}{R_b A}$), Where σ_T is the ionic conductivity of the electrolyte, l is the thickness of the gel electrolyte, A is the contact surface area of the gel electrolyte, and R_b represents the electrolyte bulk resistance, which can be obtained from the intercept on the real axis of the EIS Nyquist plot [50]. **Table 8** summarizes the data obtained from the EIS analysis. **Figure 27a** below represents the EIS Nyquist plot from the EIS analysis of the hydrogel electrolyte. The contact area of the electrolyte is 5 cm^2 , while the thickness of the electrolyte is 0.682 cm . Based on the above data, we calculated the ionic conductivity and summarize them in table 1. **Figure 27b** represent the ionic conductivity of the DSDC-NaOH-Urea electrolyte at different temperatures.

Table 8: Summary of Bulk resistance and ionic conductivity as a function of temperature.

Temperature (°C)	Bulk resistance (R _b) (Ohm)	Ionic conductivity (mS/cm)
25 (RT)	5.8	23.5
40	3.7	36.7
60	3	45.5
80	2.7	50.5

5.4.2 Linear sweep voltammetry (LSV)

Furthermore, LSV in two electrode systems was conducted to determine the operating potential window (OPW) of the electrolyte. The OPW is a crucial parameter for an electrolyte, as it establishes the maximum operating voltage limit for electrochemical energy storage devices such as batteries and supercapacitors [270]. **Figure 27c** shows the LSV curve of the DSDC-NaOH-Urea conducted at 100 mV/s from -3 to 3 V. According to the curve, the OPW was found to be approximately 4 V (from -2 to +2) indicating high stability of the electrolyte. This means that our developed electrolyte is free from decomposition at high potential which is the major drawback of aqueous based electrolytes.

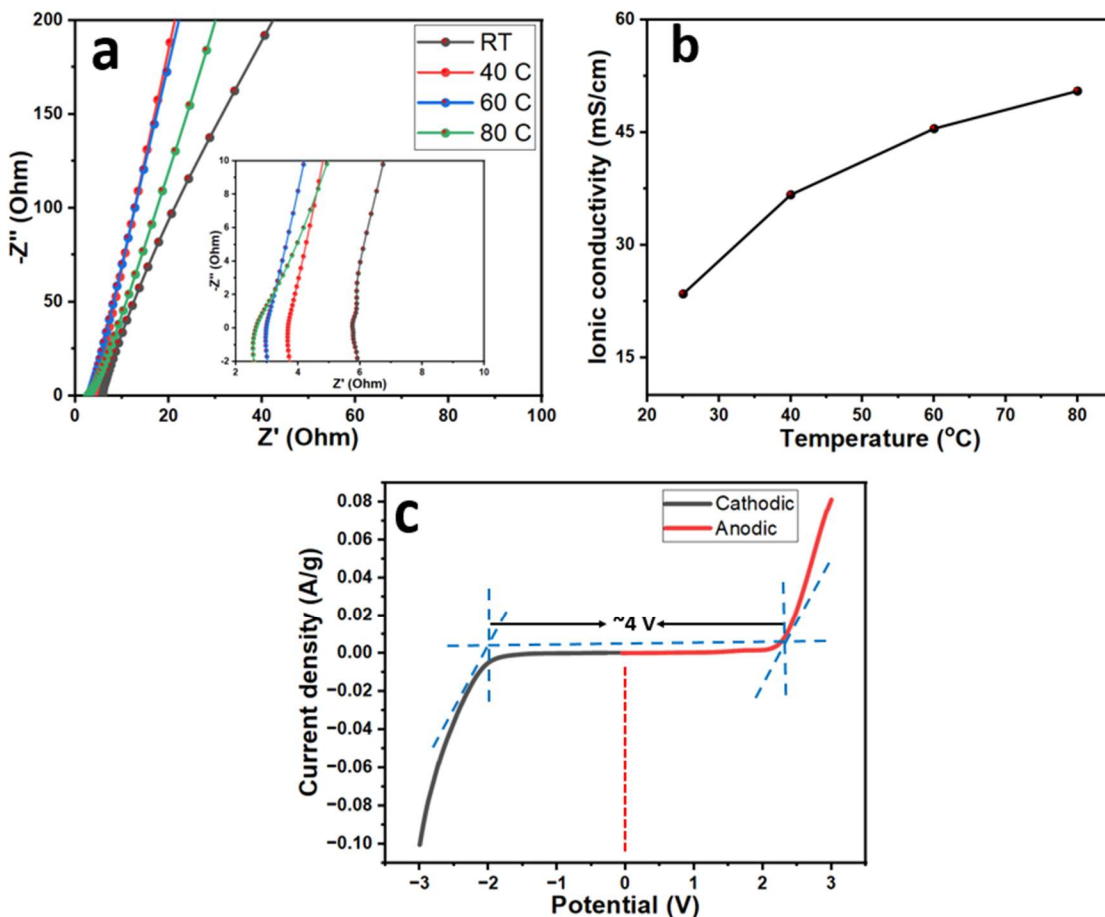


Figure 27. (a) EIS Nyquist plot of the hydrogel electrolyte at different temperatures (insert is the magnified image), (b) Ionic conductivity at different temperatures, (c) LSV spectra, indicating the stable OPW of the electrolyte.

5.4.3 Cyclic voltammetry (CV)

For further electrochemical performance evaluation, CV was conducted at different potential windows. The voltammogram shown in **Figure 28a** represents the CV data recorded at different potential window from 0 to 2 V at constant scan rate of 100 mV/s. The voltammograms shows quasi rectangular shape up to 1.8 V, however, beyond this threshold, a substantial deviation in the CV shape is observed. Therefore, the optimized voltage range for further studies has been selected up to 1.8 V. **Figure 28b** represents the CV spectra of the assembled supercapacitor at different scan rates of 10 to 150 mV/s from 0 to 1.8 V. The CV curve indicates a typical EDLC behavior where the charge storage

mechanism is based on the adsorption and desorption of ions on the surface of the activated carbon electrode. **Figure 28c** shows the specific capacitance calculated from the CV curve as a function of scan rates using **equation 1** . As expected, lower scan rate correspond to higher specific capacitance. This is because, at low scan rate, the electrolyte ions are given enough time to penetrate the porous network of the activated carbon electrodes, thereby resulting in the accumulation of large amounts of ions on the activated carbon electrodes, which results in high specific capacitance [259]. Conversely, at higher scan rates, the specific capacitance appear to be low. This is due to fact that, high scan rates left the ions with limited time to penetrate the porous network of the activated carbon, which results in few numbers of ions on the electrode surface, which is in turn reflected on the overall performance of the supercapacitor [259].

$$C_s = \frac{\int I \times \Delta V}{m \times v \times \Delta V} \quad (1)$$

$$C_s = \frac{I \times \Delta t}{m \times \Delta V} \quad (2)$$

$$E = \frac{1}{2} \frac{C_s \times \Delta V^2}{3.6} \quad (3)$$

$$P = \frac{E \times 3600}{\Delta t} \quad (4)$$

Where $\int I \times \Delta V$ represents the area under the CV curve, in watts, m denotes the average mass of the active material on both electrodes, in grams, v is the scan rate, in V/s, ΔV is the OPW in volt, I is the applied current in ampere, Δt is the discharge time in seconds, C_s is the specific capacitance in F/g, E is the energy density in Wh/kg, and P is the power density in W/kg.

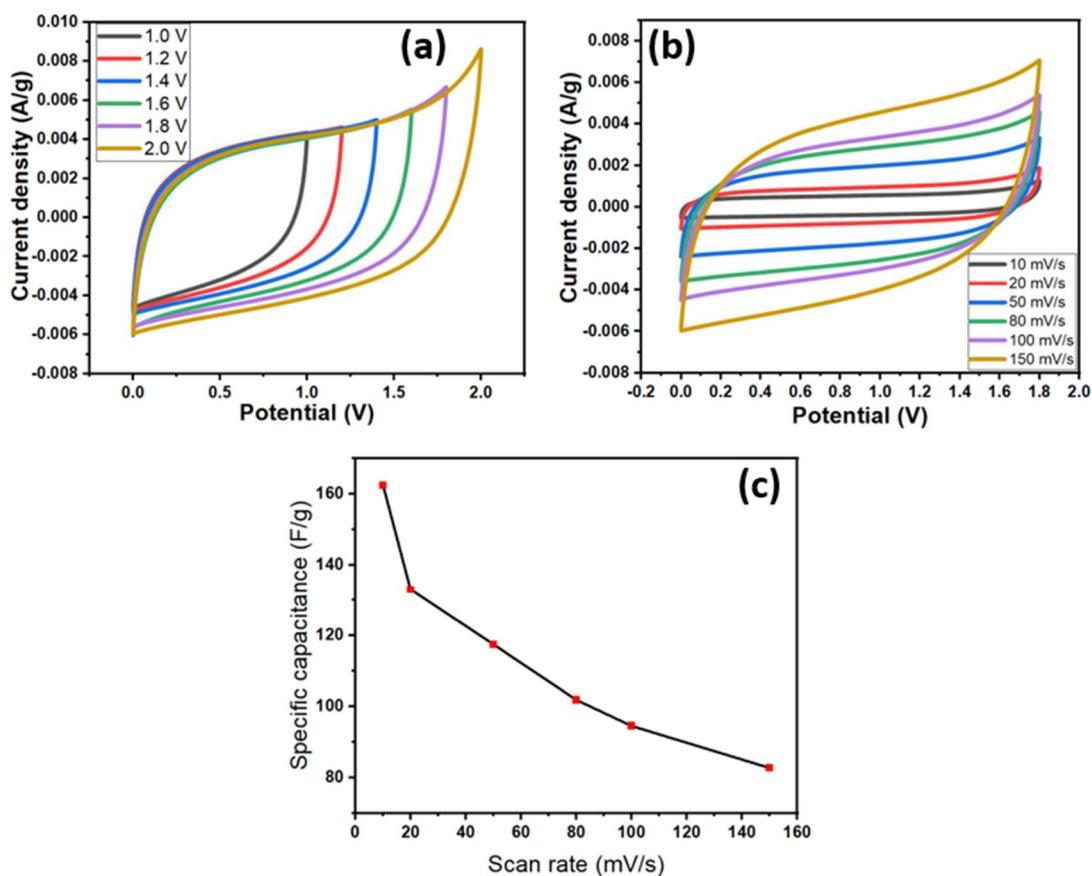


Figure 28. (a) CV spectra at different potential window, (b) CV spectra at different scan rates, and (c) specific capacitance as a function of scan rates for the assembled supercapacitor.

5.4.4 Galvanostatic charge/discharge (GCD)

To further evaluate the performance of the supercapacitor, we recorded GCD at different potential window from 0 to 2 V, at constant current density of 2 A/g. As shown in **Figure 29a**, the assembled supercapacitor is stable up to 1.8 V. Above 1.8 V, a significant departure from the linear capacitive pattern in the GCD analysis was observed and therefore, the optimum operating potential window for the supercapacitor was chosen to be 1.8 V for further investigations. **Figure 29b** shows the GCD spectra at different current densities of 0.5 to 5 A/g and potential window of 0 to 1.8 V was employed. **Equation 2** was used to calculate the specific capacitance at different scan rates which were summarized in **Figure 29c**. The highest specific capacitance attained by our developed

supercapacitor is 113.75 F/g at 0.5 A/g and remains as high as 56.25 at high current density of 5 A/g. This result indicates that date stone biomass has a great potential in the development of high performance supercapacitors.

Energy and power density are two key parameters that determine the performance of supercapacitors. Therefore **equations 3 and 4** [259] were used to calculate the energy and power density of the assembled supercapacitors. **Figure 29d** is called Ragone plot, which is a summary of the energy density as a function of the power density. According to the plot, the energy density is inversely proportional to the power density. The highest energy density attained by our assembled supercapacitor is 40.44 Wh/kg at 400 W/kg, and it remain as high as 20 Wh/kg at high power density of 4000 W/kg.

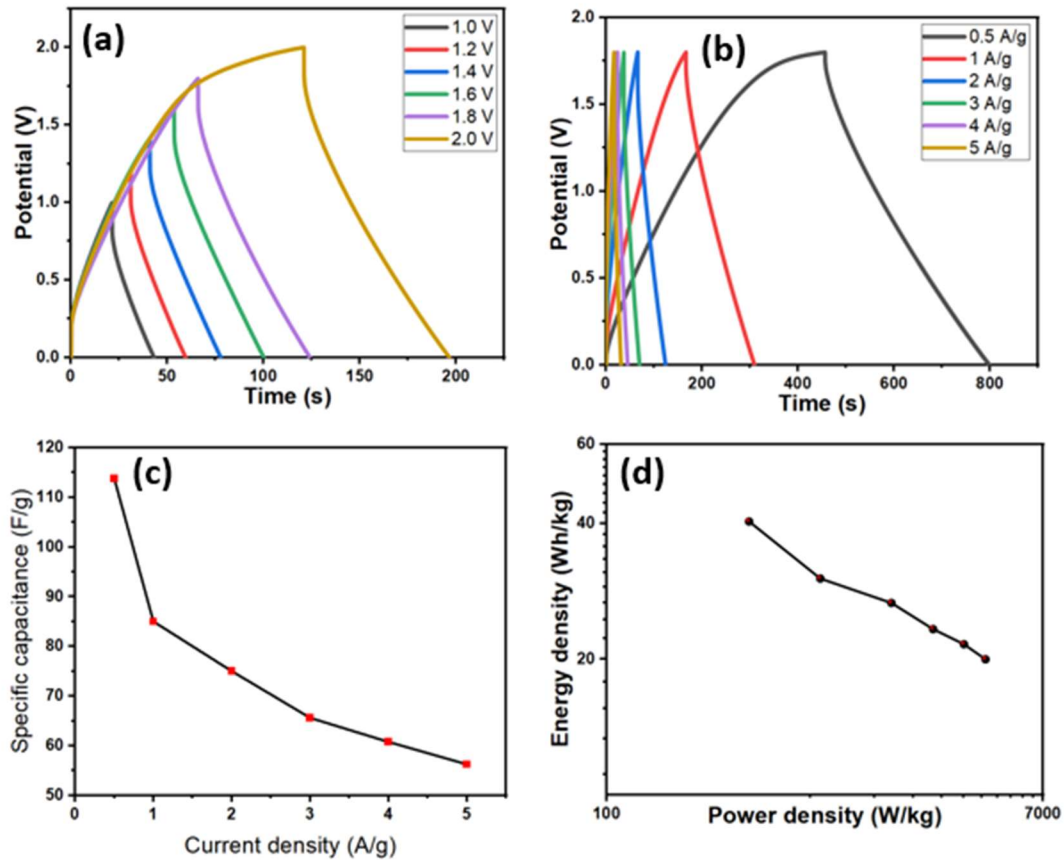


Figure 29. (a) GCD spectra at different potential window, (b) GCD spectra at different current density, (c) specific capacitance as a function of current densities, and (d) Ragone plot.

3.4.5 Performance evaluation and Electrochemical impedance spectroscopy (EIS)

Figure 30a represents the performance evaluation of the assembled supercapacitor for 5000 cycles. The cycling stability was carried out at high current density of 10 A/g. After 5000 cycles, the capacitance retention was 107.42% and the columbic efficiency was 100%. This result suggests high cycling stability and a high degree of charge-discharge reversibility of the assembled supercapacitor. Electrochemical impedance spectroscopy was employed to study the interfacial properties of the assembled supercapacitor before and after the stability test. **Figure 30b** compares the Nyquist plot of the before and after 5000 cycles. The bulk resistance of the supercapacitor, which consist of the electrode and electrolyte was obtained from the real axis of the Nyquist plot [259], while the diameter of the compressed semi-circle is called the interfacial resistance; which is the resistance that arises from the contact between the electrode and electrolyte. From the graph, the bulk resistance of the supercapacitor before cycling was found to be approximately 0.8Ω while the interfacial resistance is negligible. Moreover, after 5000 cycles, there is a significant increase in the interfacial resistance, and it may be attributed to the high amount of current applied during the long cycling which may cause the electrolyte to decompose that affect the ionic conductivity and leads to increased resistance. Additionally, no significant variation was observed in the bulk resistance.

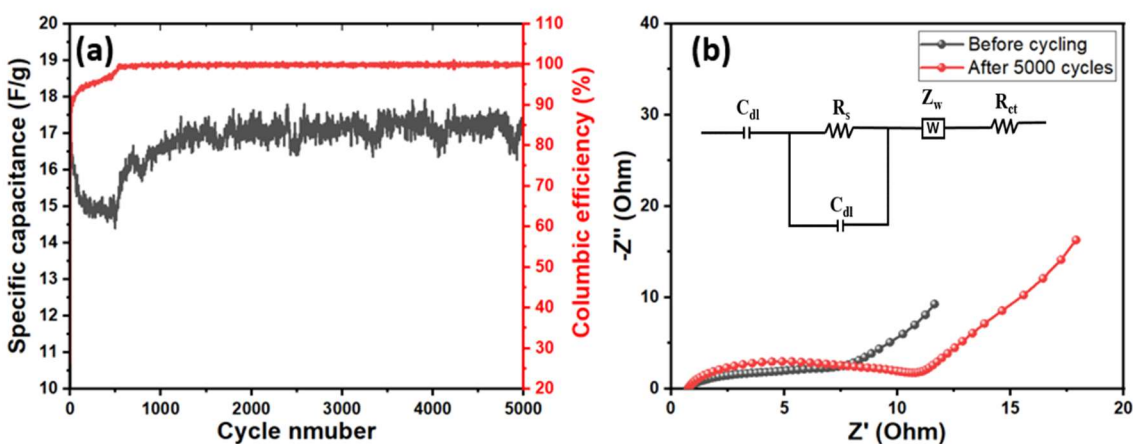


Figure 30. (a) Cycling performance, (b) EIS Nyquist plot before and after 5000 cycles (insert is the equivalent circuit model).

5.4.6 Temperature dependent performance

Furthermore, we evaluated the performance of the supercapacitor at different temperatures. The temperature-dependent analysis is very important as it will determine the applicability of the device within a wide range of temperatures (from room temperature to 50 °C). CV, GCD, and EIS were performed at different temperatures. The CV was carried out at constant scan rate of 100 mV/s while the GCD was done at constant current density of 2 A/g. As shown in **Figure 31a-c**, the performance of the supercapacitor improved as the temperature increased. This is because ionic conductivity is directly proportional to temperature. This means that as the temperature increases, the ionic conductivity increases which leads to decrease in resistance and leading to increase in overall electrochemical performance.

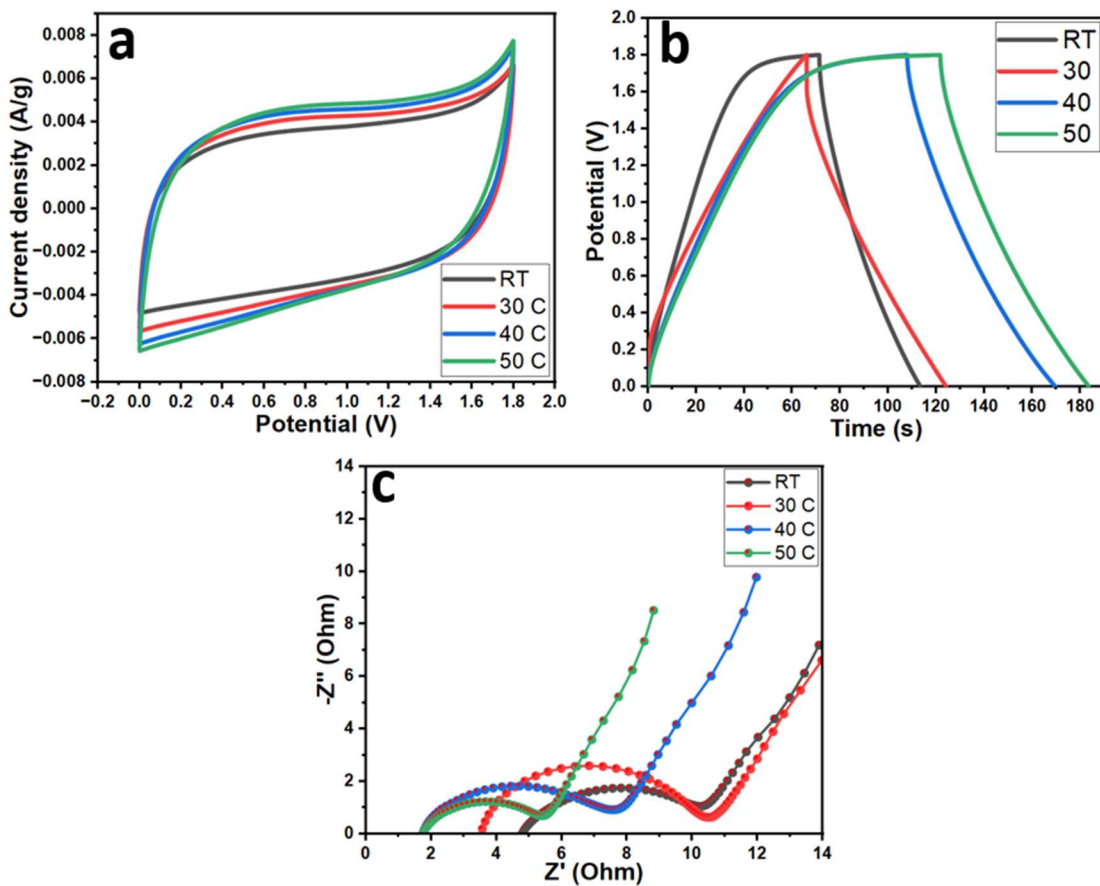


Figure 31. (a) CV at different temperatures and a scan rate of 100 mV/s, (b) GCD at different temperatures and a current density of 2 A/g, (c) EIS spectra at different temperatures.

5.5 Conclusion

We have successfully for the first time developed an all-biomass supercapacitor based on date stone biomass. The supercapacitor demonstrated impressive electrochemical characteristics including high specific energy of 40.44 Wh/kg at a specific power of 400 W/kg remaining as high as 20 Wh/kg at 4000 W/kg, attaining a wide operating potential window (OPW) of 1.8 V, excellent cycle stability with 107.42% capacitance retention and ~100% columbic efficiency after 5000 cycles. The research demonstrate the potential of date stone for energy storage application and serve as an avenue for further research in this field. Furthermore, this research has great implication on the economy of Saudi Arabia as it serves as a platform for the development of cost effective and environmentally-friendly materials for energy storage applications.

CHAPTER 6

CONCLUSION AND FUTURE PERSPECTIVES

6.1 Conclusion

In summary, we have successfully fabricated three supercapacitors. SC 1 was successfully constructed using the DSAC and anthraquinone-based redox gel electrolyte (PVA-H₂SO₄-AQ), and its electrochemical performance was investigated. The SSC displays impressive performance, with a high specific capacitance of 126.5 F/g, an energy density of 17.5 Wh/kg at a power density of 250 W/kg, and 87% capacitance retention after 1000 continuous GCD cycles. SC 2 fabricated using PVA-Li₂SO₄-IL gel membrane electrolyte exhibits a high energy density of 65.14 Wh/kg and attains a high operating voltage window of 2V and high specific capacitance of 116.25 F/g at 0.5 A/g. It also shows high cycling stability with 87.7% capacitance retention and coulombic efficiency of approximately 100% after 10000 cycles. SC 3 developed from date stone demonstrated impressive electrochemical characteristics including high specific energy of 40.44 Wh/kg at a specific power of 400 W/kg remaining as high as 20 Wh/kg at 4000 W/kg, attaining a wide operating potential window (OPW) of 1.8 V, excellent cycle stability with 107.42% capacitance retention and ~100% columbic efficiency after 5000 cycles. To meet the growing demand for high-performance energy storage devices, we developed a simple and effective method for fabricating supercapacitors using a strong redox-active gel polymer electrolytes and biomass-derived activated carbon. Consequently, the potential of these innovative electrolytes in enhancing the electrochemical performance of energy storage devices is highly promising. Furthermore, their application in various other electrochemical domains can be expedited, contributing to further advancements in the field of electrochemistry and energy storage in general.

Appendix

Table 9. Electrochemical impedance parameters from the equivalence circuit of PVA-H₂SO₄-AQ supercapacitor.

Table	Circuit	$R_s (\Omega \text{ cm}^2)$	$R_{ct} (\Omega \text{ cm}^2)$	$C_{dl} (\Omega \text{ cm}^2)$	$C_{dl} (\Omega \text{ cm}^2)$	$Z_w (\text{F cm}^{-2})$
components						
Value		1.842	0.8224	0.06349	4.276e-5	0.1001

Table 10. Electrochemical impedance parameters from the equivalence circuit PVA-Li₂SO₄-AQ supercapacitor.

Table	Circuit	$R_s (\Omega \text{ cm}^2)$	$R_{ct} (\Omega \text{ cm}^2)$	$C_{dl} (\Omega \text{ cm}^2)$	$C_{dl} (\Omega \text{ cm}^2)$	$Z_w (\text{F cm}^{-2})$
components						
Value		1.843	0.8225	0.06335	4.276e-5	0.1002

Table 11. Electrochemical impedance parameters from the equivalence circuit DSDC-NaOH-Urea supercapacitor.

Table	Circuit	$R_s (\Omega \text{ cm}^2)$	$R_{ct} (\Omega \text{ cm}^2)$	$C_{dl} (\Omega \text{ cm}^2)$	$C_{dl} (\Omega \text{ cm}^2)$	$Z_w (\text{F cm}^{-2})$
components						
Value		1.724	0.828	0.06349	3.768e-5	0.07617

R_s : ohmic series resistance; R_{ct} : charge-transfer resistance; C_{dl} : electric double-layer capacitance; and Z_w : Warburg impedance.

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Publications:

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- Composites of Biomass-Derived Materials and Conducting Polymers; Wiley Online Library; <https://doi.org/10.1002/9781119866435.ch20>
- Metal Negatrode Supercappatteries: Advancements, Challenges, and Future Perspectives for High-Performance Energy Storage; *The Chemical Record*; <https://doi.org/10.1002/tcr.202300239>
- Synthesis and Performance Evaluation of a Novel Gel Membrane Electrolyte Prepared from Polyvinyl Alcohol, Li_2SO_4 , and 1-Butyl-3-Methylimidazolium Trifluoromethansulfonate for High-Performance Supercapacitors (accepted).
- Advancing Gel Polymer Electrolytes for Next-Generation High-Performance Solid-State Supercapacitors: A Comprehensive Review on Innovations, Obstacles, and Prospects (under review).
- All-biomass Supercapacitors with Date Stone-Derived Activated Carbon Electrodes and Cellulose Hydrogel Electrolyte (under preparation).