Research article

SCOBY-based bacterial cellulose as free standing electrodes for safer, greener and cleaner energy storage technology

Muhamad Hafiz Hamsana, Norhana Abdul Halima,*, Siti Zulaikha Ngah Demonab, Nurul Syahirah Nasuha Sa’ayac, Mohd Fakhrul Zamani Kadiid,e, Zul Hazrin Zainal Abidinf, Nursaadah Ahmad Poadf, Nurul Farhana Abu Kasimg, Nur Amira Mamat Razalic, Shujahadeen B. Azizgh, Khairol Amali Ahmadh, Azizi Miskonil, Norazman Mohamad Nori

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ABSTRACT

Bacterial Cellulose (BC) derived from local market or symbiotic culture of bacteria and yeast (SCOBY) was employed as the polymer matrix for hydroxyl multi-walled carbon nanotube (MWCNT-OH)-based electrochemical double-layer capacitor (EDLC). Chitosan (CS)-sodium iodide (NaI)-glycerol (Gly) electrolyte systems were used as the polymer electrolyte. CS-NaI-Gly electrolyte possesses conductivity, potential stability and ionic transference number of (1.20 x 10^-3 Sc m^-2, 2.5 V and 0.99, respectively. For the electrodes, MWCNT-OH was observed to be well dispersed in the matrix of BC which was obtained via FESEM analysis. The inclusion of MWCNT-OH reduced the crystallinity of the BC polymeric structure. From EIS measurement, it was verified that the presence of MWCNT-OH decreased the electron transfer resistance of BC-based electrodes. Cyclic voltammetry (CV) showed that the shape of the CV plots changed to a rectangular-like shape plot as more MWCNT were added, thus verifying the capacitive behavior. Various amount of MWCNT-OH was used in the fabrication of the EDLC where it was discovered that more MWCNT-OH leads to a better EDLC performance. The EDLC was tested for 5000 complete charge-discharge cycles. The optimum performance of this low voltage EDLC was obtained with 0.1 g MWCNT where the average specific capacitance was 8.80 F g^-1. The maximum power and energy density of the fabricated EDLC were 300 W kg^-1 and 1.6 W h kg^-1, respectively.

1. Introduction

Demand in electrical gadgets, machinery and vehicles technologies keep on increasing every year due to human nature of finding an easier and comfortable living. This vision can be achieved along with technology that is safe and clean for the environment [1]. Most heavy machinery and vehicles run with ton of liquid fossil fuels. Without no doubt, fossil fuels have been the number one choice by most countries due to its efficiency. However, carbon emissions from fossil fuel trap heat in the atmosphere which is clearly the main source of climate change. Problems faced in fossil fuels consumption e.g. supply risk, scarcity, unpredictable markets and prices have diverted the world to low carbon economies [2]. Despite all the challenges, the world still needs to move forward, thus a lot of energies are required in the future. Due to the extreme demand of energy sources, various types of sustainable and renewable energy have been developed in the past few decades such as biomass from municipal
solid waste, wood paste, landfill gas, biogas [3], solar [4], hydropower [5], wind [6], geothermal [7], fuel cells [8] and supercapacitors [9].

Supercapacitors (SCs) are one of the crucial key to solve our energy shortage problems as well as an important component in building an electric vehicle for big company e.g. Tesla, Karma, Lucid, Faraday Future, Brammo and Nikola. SCs can be divided into three types i.e. pseudocapacitor, electrochemical double-layer capacitor (EDLC) and hybrid capacitor [10]. Pseudocapacitor holds a faradic process for the energy storage mechanism where typically metal oxide and conducting polymer are employed as the electrodes as it relies on redox reaction. Normally in pseudocapacitor, there will be a redox reaction in the energy storage mechanism [11]. Unlike pseudocapacitor, EDLC possesses non-Faradic current response where the polarization of charges happens on the surface of identical carbon-based electrodes. No redox reactions require in the process of energy storage in EDLC [12]. Lastly, when both energy storage mechanisms of pseudocapacitor and EDLC are combined together, the devices now are called as hybrid capacitor [13]. Between these capacitors, EDLC has the easiest fabrication method as well as excellent life cycle, flexible, light in weight and high power density [14].

The most famous material used in energy storage technologies is carbon. Carbon-based SCs have been explored due to its fast pulses of energy, wide operating temperature, high power, large cycle number and better performance. Carbon-based SCs have been employed as the electrodes as it relies on redox reaction. Normally in pseudocapacitor, there will be a redox reaction in the energy storage mechanism [11]. Unlike pseudocapacitor, EDLC possesses non-Faradic current response where the polarization of charges happens on the surface of identical carbon-based electrodes. No redox reactions require in the process of energy storage in EDLC [12]. Lastly, when both energy storage mechanisms of pseudocapacitor and EDLC are combined together, the devices now are called as hybrid capacitor [13]. Between these capacitors, EDLC has the easiest fabrication method as well as excellent life cycle, flexible, light in weight and high power density [14].

The most famous material used in energy storage technologies is carbon. Carbon-based SCs have been explored due to its fast pulses of energy, wide operating temperature, high power, large cycle number and good coulombic efficiency [15]. Various modification of carbons e.g. carbon nanogel (CN), activated carbon (AC), carbon nanotubes (CNT), graphite and graphene sheets are available for research and industry purposes [16]. Ubaidullah et al. [17] reported a high performance supercapacitor using highly porous N-doped mesoporous carbon using carbon possesses different uniqueness and advantages. Other name for CNT is carbon nanowalls. CNT have gained numerous attention owing to their morphology, excellent nanosized scale, physico-chemical properties and in their versatile applications [19]. Easy way to visualized CNT is a graphene sheets that are rolled into a cylinder sheets [20]. There are two types of CNT which is categorize based on the wall such as single-walled and multiwalled CNT. The major difference between single-walled (SWCNT) and multi-walled CNT (MWCNT) is the diameter of the cylinder in the CNT layers which are 1–2 nm and 2–25 nm, respectively. Other unique properties of CNT is that it can act as semiconductor or metal depending on the helicity and diameter [21].

A specific amount of CNT in a polymeric structure can improve the overall conductivity of the nanocomposite. This process is well known as percolation, implying on the formation of a 3D electrically conducting network within the polymer structure [22]. Deng et al. [23] the addition of 6 wt.% MWCNT into a fibrous cellulose acetate network has increased the electrical properties. CNT has been blended with various polymers e.g. CNT-polyimide [24], CNT-polyvinylidene difluoride (PVDF) [25], CNT-polyvinyl alcohol (PVA) [26], CNT-polyethylene oxide (PEO) [27], CNT-polyacetic acid (PLA) [28] and many more in various applications and industries. The used of CNT as the additive is due to their excellent electrical conductivity, nucleating effect on graphitization at a low temperature and chemical stability. These make CNT good for modulating the microstructure and enhancing the capacitance [29].

Up until now human made polymers such as PVDF and polyvinylpyrrolidone (PVP) are widely used as the binder in commercial SCs and batteries. The human made binders are non-biodegradable which leads to waste problem in the future. As a long term solution, researchers are now more focusing on green alternatives polymers. Landi et al. [30] reported that EDLCs with different natural binders e.g. CS, gum, casein, gelatin and carboxymethylcellulose showed different charge-discharge performance and some of it are outstanding. BC has gained numerous attention due to their unique characteristics for instance high aspect ratio, formability, eco-friendly, excellent mechanical strength and flexible [31]. BC has ether groups (–C–O–C–) in its structure that is comparable with polyethylene oxide (PEO) which is beneficial for ionic conduction. BC has high crystallinity and purity structure thus it can produce a paper or film with excellent mechanical strength as well as flexibility [32]. Thus SCs with BC-based electrode can be incorporated in wearable cloth and devices with abnormal shapes.

The multifunctional characteristic of cellulose has caught attentions due to its possibility in various application. Kasprak et al. [33] reported a supercapacitor with specific capacitance \( C_s \) between 20 and 21 F g\(^{-1}\) using cellulose as the electrodes and hydrogel electrolytes. An EDLC with cellulose nanofibril-based electrodes by Tanguy et al. [34] can be charged and discharged for 5000 cycles. The authors claimed that cellulose enables the possibilities of fabricating a flexible energy device due to its outstanding properties. Kotatha et al. [35] have fabricated a BC-based EDLC with CS and alginate coating and obtained capacitance retention from 45.6 to 60.7%. The authors stated that the concentration of ionic liquid plays an important role in developing a high performance EDLC. A BC-based hybrid capacitor by Xu et al. [36] can be charged and discharged for complete 5000 cycles with power density \( P_d \) of 276 W kg\(^{-1}\). The authors also mentioned that energy density \( E_d \) of their capacitor is affected by the changes in power density.

In this work, we used biopolymer electrolyte with CS as the polymer host due to their excellent film forming properties. NaI and glycerol are used as the ionic source and plasticizer, respectively. For the electrolyte, crucial electrical analyses e.g. transference number (TNN), linear sweep voltammetry (LSV) and electrochemical impedance analysis (EIS) are done. For the electrodes, BC acts as the binder to form a flexible paper while CNT is used as the active material for polarization process. Various MWCNT-BC electrodes have been prepared with different amount of MWCNT. Thus, few EDLCs have been fabricated using MWCNT-BC electrodes. The correlation between MWCNT-BC ratio and important parameters for the fabricated EDLC such as \( C_p \), equivalent series resistance (\( R_{eq} \)), \( P_d \), \( E_d \) and efficiency are the main focus in this work.

2. Experimental procedures

2.1. Materials

CS, NaI, MWCNT-ÖH (conductivity, \( S = 107 \) S m\(^{-1}\)) and sodium dodecyl sulfate were procured from Sigma-Aldrich while glycerol was purchased from SYSTERM. Acetic acid was purchased from Friend-emann Schmidt. Source of cellulose is a type of bacterial cellulose (BC) hydrogel obtained from local market (Malaysia).

2.2. Preparation of CS-NaI-Gly electrolyte

A total of 1 g CS powder was dissolved in 1 % acetic acid (100 mL) using a magnetic bar at 298 K for 6 h and 40 wt.% NaI was doped into the CS solution. CS-NaI solution was stirred for several 2 h for complete dissolution. Glycerol (40 wt.%) was then added into CS-Nal solution where it was stirred for 2 more hours. The final electrolyte solution was poured into a Petri dish and dried at room temperature in a fume hood. The formed films were stored in a desiccator prior to any characterizations.

2.3. Characterizations of CS-NaI-Gly electrolyte

The thickness \( d \) of CS-NaI-Gly film was measured using Mitutoyo micrometer screw gauge. The thickness of CS-NaI-Gly film was maintained at 0.02 cm for better EDLC comparison purposes. An impedance spectroscopy (HIOKI 3532–50 LCR) was set from 50 Hz to 5 MHz, in order to identify the bulk resistance of the electrolyte \( R_b \). The film was placed between two stainless steel surfaces of a Teflon case. The conductivity \( \sigma \) was obtained via the following equation [1]:

\[
\sigma = \frac{d}{AR_b}
\]
The ionic \( (t_i) \) and electronic \( (t_e) \) and transference number \( (TNM) \) were obtained using V&A instrument DP3003 digital DC power supply connected to a multimeter. The working voltage for the polarization process was 0.2 V. The analysis was conducted at room temperature which \( t_i \) was calculated using the following equations [9]:

\[
t_i = \frac{I_i - I_o}{I_i}
\]

The initial and stable current reading were set as \( I_i \) and \( I_o \) respectively, where the summation of \( t_i \) and \( t_e \) is equal to 1. The potential stability of CS-NaI-Gly films was analyzed using linear sweep voltammetry (LSV) measurement. In this analysis, potential was swept linearly from 0 to 3 V. This analysis was done using a potentiostat (Digi-IVY DY2300) at a slow scan rate of 1 mV s\(^{-1}\).

2.4. Preparation of MWCNT-BC (BXC) electrodes

MWCNT solution was prepared by dispersing 0.05 mg of MWCNT-OH with 20 mL of deionized water. This dispersion was sonicated for 20 min in ultrasonic bath. Meanwhile, 3.0 g of BC was filtered using manual filtration before adding the filler. MWCNT-OH and BC were then blended with deionized water using a magnetic stirring process at 45 °C for 24 h until the homogenous solution was achieved. The homogenous BXC solution was then vacuum-filtered using a Buchner funnel. Different amounts of MWCNT-OH were used e.g. 0.1 g, 0.075 g, 0.05 g, and 0.025 g, where the designations were set as BXC0.1, BXC0.075, BXC0.05, and BXC0.025, respectively. Finally, the produced BXC nanocomposites electrodes were peeled off and dried at room temperature for further characterization.

2.5. Characterizations of BXC electrodes

In order to confirm the complexation of BC and MWCNT, X-ray diffraction (XRD) analysis was done using Bruker Model X-Ray Diffractometer Bruker Model. The 20 range in this study was from 5° to 50° at a step size of 0.002°. FESEM analysis was done to observe the structural changes of BC’s surface where Gemini SEM500 instrument was used at a resolution of 50k×.

2.6. Fabrication of EDLC

BXC electrodes was cut into a small circle with area of 2.01 cm\(^2\). The CS-Nal-Gly was sandwiched between two identical BXC electrodes which then packed in a CR2032 coin cell. The coin cell was pressed using a battery clapper. The pressed coin cell was placed in a Teflon case for further analysis. The illustration of the fabricated EDLC can be seen in Figure 1.

2.7. Characterization of the fabricated EDLC

Cyclic voltammetry measurement was used to check any redox reaction in the potential range used in this work. Digi-IVY DY2300 potentiostat was used for this analysis where various scan rates e.g. 5, 10, 20 and 50 mV s\(^{-1}\) were used. The capacitance \( (C_{cv}) \) of the fabricated EDLC can be obtained via CV analysis using following equation [25]:

\[
C_{cv} = \frac{\int V f(V) dV}{2(V_f - V_i)x}
\]

where \( I(V) \) is the area of CV plot, \( x \) represents the scan rate and \( m \) is mass of active material which in this case, the mass of MWCNT-OH. \( V_f \) and \( V_i \) are the final and initial voltage, respectively.

The charge-discharge analysis was performed using NEWARE battery cycler with the current density of 0.75 mA cm\(^{-2}\). Crucial parameters of the EDLC, for example specific Cs, Rs, \( P_d \), \( Ed \), and efficiency [9]:

\[
Cs = \frac{i}{gm} \quad (4)
\]

\[
R_{so} = \frac{V_d}{i} \quad (5)
\]

\[
E_d = \frac{C_i V^2}{2} \quad (6)
\]

\[
P_d = \frac{V^2}{4mR_{so}} \quad (7)
\]

where \( g \) is the slope of discharge part, \( V_d \) stands for the potential drop and \( i \) is the working current which was 1.5 mA.

3. Results and discussion

3.1. CS-Nal-Gly electrolyte study

3.1.1. Conductivity and impedance analysis

Figure 2 shows the Nyquist plot for CS film, CS-Nal film and CS-Nal-Gly. CS film shows an incomplete semicircle where this semicircle is due to ionic conduction in the bulk of electrolyte.

![Figure 1. Schematic diagram of the fabricated EDLC.](image-url)
As 40 wt.% NaI is added into CS film, the diameter of the semicircle has become smaller with a tilted spike. Tilted spike can be seen at high salt concentration as more ions can form charge double layer or polarization [37]. Addition of plasticizer, in this case glycerol, creates more pathways for ionic conduction as well as lowering the columbic contact between ions [38]. This explains the disappearance of semicircle and only tilted spike can be observed as 40 wt.% glycerol is added.

**Figure 2.** The Nyquist plot of (a) CS film, (b) CS-NaI film and (c) CS-NaI-Gly.

**Figure 3.** LSV plot of CS-NaI-Gly electrolyte at 1 mV s⁻¹.

**Figure 4.** Polarization curve of CS-NaI-Gly electrolyte at 0.2 V.

**Figure 5.** XRD spectrum of BC, BXC and MWCNT.

As 40 wt.% NaI is added into CS film, the diameter of the semicircle has become smaller with a tilted spike. Tilted spike can be seen at high salt concentration as more ions can form charge double layer or polarization [37]. Addition of plasticizer, in this case glycerol, creates more pathways for ionic conduction as well as lowering the columbic contact between ions [38]. This explains the disappearance of semicircle and only tilted spike can be observed as 40 wt.% glycerol is added.

**Table 1.** Peaks position and their respective lattice plane (hkl).

| Lattice plane (hkl) | 2θ (°) 001 | 2θ (°) 110 | 2θ (°) 002 | 2θ (°) 100 |
|---------------------|------------|------------|------------|------------|
| BC                  | 14.18      | 16.23      | 22.41      | -          |
| MWCNT               | -          | -          | 25.70      | 43.45      |
| BXC                 | 14.03      | 22.24      | 25.73      | 43.98      |
Figure 6. FESEM micrograph of (a) BC, (b) MWCNT and (c) BXC.

Figure 7. CV plot of the EDLC with (a) BXC0.025, (b) BXC0.05, (c) BXC0.075 and BXC0.1 at various scan rates.
obtained conductivity of CS film, CS-NaI film and CS-NaI-Gly film are $(7.86 \pm 4.90) \times 10^{-3}$ S cm$^{-1}$, $(4.4 \pm 0.84) \times 10^{-6}$ S cm$^{-2}$ and $(1.20 \pm 0.26) \times 10^{-3}$ S cm$^{-2}$, respectively. Due to the high ionic conductivity of CS-NaI-Gly film, it can be used as the electrodes separator. In order to make an electrolyte useful in energy storage devices, the conductivity must be at least $\sim 10^{-3}$ S cm$^{-2}$ [39]. The spike in the Nyquist plot of the glycerolized electrolyte showed that high polarization happens at the surface of the electrodes.

3.1.2. Potential stability analysis

In EDLC application, the device normally undergoes rapid charge-discharge process in a safe potential range. Safe potential range can avoid the breakdown of polymer electrolyte thus it can be used for longer charge and discharge cycles. The purpose is to spot at which potential the polymer electrolyte will be oxidized or reduced and eventually degraded [40]. Figure 3 shows the LSV plot for CS-NaI-Gly electrolyte at room temperature. As the potential swept linearly from 0 to 2 V, no obvious changes in current can be seen. The stable current before 2 V is associated with the capacitive current as electrochemical double layer formed at the surface of the stainless steel electrodes. A slight increase in current is noticeable as the potential exceeded 2 V. This signifies that the redox reaction has started to occur beyond 2 V. Beyond 2.5 V, a sharp increment in current value can be observed. This current is a faradaic current response due to the redox reaction within CS-NaI-glycerol electrolyte. Thus it is safe to use CS-NaI-glycerol electrolyte as the electrode separator of the EDLC up to 2 V.

3.1.3. Transference number analysis (TNM)

A good electrodes separator or electrolyte for an EDLC must have a high ionic transference number in view of the fact that ions act as counterions that form electrostatic force with carbon electrodes. In this work, $Na^+$ and $I^-$ are the main charge-carrying species and electron as the less dominance charge carrier. In order to verify this statement, TNM analysis is conducted as portrayed in Figure 4. The current is high (10.4 $\mu$A) and unstable at the beginning of the plot. At this point, ions move towards the electrodes and ions that are near to electrodes form electrical double layer. After several seconds, the current value drops and stabilize where complete polarization is achieved. The obtained $\tau_i$ and $\tau_e$ are 0.99 and 0.01, respectively. $\tau_i$ is close to unity signifying the dominancy of ion as charge carrier. The finding is comparable to other Na-based electrolytes e.g. PVA-Nal-Gly (0.98) [41], PVA-Nal (0.954–0.974) [42], and CMC-NaNO$_3$ (0.97) [43].

3.2. BC:MWCNT (BXC) electrodes study

3.2.1. XRD analysis for BXC electrodes

In order to observe the changes and complexation in the structure of BC electrodes, XRD analysis has been conducted and can be seen in Figure 5. It is noticeable that BC has two distinguishable crystalline at $2\theta = 14.18^\circ$ and 22.41$^\circ$ along with a small shoulder peak at $2\theta = 16.23^\circ$. These three peaks are common native peaks for a cellulose [44]. This outcome is comparable to other reported BC-based film studies [45, 46]. Meanwhile for MWCNT, only two obvious peaks can be observed at $2\theta = 25.70^\circ$ and 43.45°. These two recognizable peaks represent the characteristic of graphite peak and attributed to the planes of the nanotube structure, respectively [47]. As BC and MWCNT are blended together all for peaks e.g. $2\theta = 14.03^\circ$, 22.24$, 25.73^\circ$ and 43.98° correspond to BC and MWCNT can be observed in BXC. Major reduction in the intensity of BC peaks at $2\theta = 14.18^\circ$ and 22.41° and slight decrement in intensity of MWCNT at $2\theta = 25.7\alpha$ and 43.45° can be seen in BXC spectrum. This verifies the complexation and interaction among BC and MWCNT. Table 1 shows the peaks position and their respective lattice plane (hkl).

3.2.2. Surface morphology study for BXC electrodes

The surface micrographs of BC, MWCNT and BXC are presented in Figure 6. Figure 6a shows that BC has random-in-plane weblike network structure of cellulose fiber of width ranging from 50 to 200 nm. BC in work also possesses a dense and compact structure with less visible pores. This outcome is in a good agreement with other reported BC study [48]. Meanwhile, for MWCNT in Figure 6b, it has a curved fibrous structure that is tangled together. The width of MWCNT fiber in this work is ranging between 20 and 50 nm. This result is comparable with the one reported by Hashimoto [49]. Figure 6c shows the structure BXC where it

| Table 2. BXC with different MWCNT amount with their respective specific capacitance from CV. |
|-----------------------------------------------|
| Scan rates/Electrodes | $C_{cv}$ (F g$^{-1}$) | $C_{cc}$ (F g$^{-1}$) | $C_{cv}$ (F g$^{-1}$) | $C_{cc}$ (F g$^{-1}$) |
|------------------------|---------------------|---------------------|---------------------|---------------------|
| 50 mV s$^{-1}$          | BXC0.025            | 0.69                | 3.52                | 5.91                | 5.71                |
|                        | BXC0.05             | 1.34                | 4.78                | 6.93                | 8.14                |
|                        | BXC0.075            | 2.02                | 6.42                | 7.48                | 9.01                |
|                        | BXC0.1              | 2.78                | 7.77                | 7.94                | 10.6                |

Figure 8. Charge-discharge curves at a selected cycle for each BXC electrodes.
can be seen that MWCNT is well dispersed in the BC network. The presence of MWCNT makes the structure of BC to be less compact. This indicates homogenous incorporation of MWCNT in the BC network where it is harmonized with XRD result.

3.3. EDLC study

3.3.1. CV analysis

CV analysis enables us to identify the type of charge storage mechanism. Typical EDLC will have a rectangular shape like plot with absence of redox peaks as the process of charge storage only happen at the surface of the electrodes via electrostatic force [50]. Various scan rates are used in this analysis to see the effect of scan rates on the CV shapes as well as the specific capacitance of the EDLC. It is well known that a capacitor is scan rate-dependent. Figure 7 displays the CV plots of the fabricated EDLC. It is noticeable that there are no obvious redox reaction peaks in all fabricated EDLC. Jackel et al. [51] claimed that a peak in CV plot typically indicates the existence of intercalation and deintercalation which is not dominant in an EDLC. Other than that, the shape of CV plot transformed to a more rectangular shape as the scan rate reduces as well as more MWCNT is added. The shapes of BXC0.1, BXC0.075 and BXC0.05 are more rectangular than BXC0.025. The rectangular and symmetry shape of the CV curves signifies the ideal electrical double layer capacitive behavior, meanwhile leaf shape indicates a large equivalent series resistance which can reduce the overall performance of the EDLC especially power density [52].

The calculated $C_{cv}$ values for each BXC electrodes are tabulated in Table 2. EDLC with low amount of MWCNT possesses lower $C_{cv}$ value.

Figure 9. Images of (a) yellow LED and (b) red LED powered by SCOBY-based supercapacitors connected in a series.
compared to the one with more MWCNT. High amount of MWCNT provides more sites for ions from the salt which in this case are Na$^+$ and I$^-$ to form charge double-layer. As a consequence, higher capacitance is obtained [53]. Low value of $C_{cv}$ is observed at larger scan rate. At fast scanning rate, ions are unable to perform proper polarization process leading to a decrement in capacitance. While, the opposite thing happens

Figure 10. Important parameters of the fabricated EDLC which are (a) specific capacitance, (b) capacitance retention, (c) ESR, (d) power density and (e) energy density.
charged up to 2 V for 60 s and connected to red and yellow LED. At 90 s red LED still produce some dimmed light compared to yellow LED. This outcome is parallel with the known fact that yellow LED (1.9–2.1 V) has higher forward voltage than red LED (1.8–2.1 V).

All crucial parameters for EDLC are depicted in Figure 10. The capacitance is expressed by the ratio of change in the electric charge corresponding to its electric potential in a given system. A stable values of $C_i$ throughout 5000 cycles are achieved and can be seen in Figure 10a. The average $C_i$ value for BXC0.025, BXC0.05, BXC0.075 and BXC0.1 are obtained at 2.47 F g$^{-1}$, 7.62 F g$^{-1}$, 8.20 F g$^{-1}$ and 8.80 F g$^{-1}$, respectively. The addition of more MWCNT into BC has enhanced the specific capacitance due to their high electronic conductivity as well as providing sufficient space for double-layer to form. Some EDLC shows instability and reduction of $C_i$ at the first few cycles. This is attributed to the formation of ion pairs and aggregates that block the process of ion adsorption onto the surface of BXC [56]. Capacitance retention is one of the ways to discuss the stability of the EDLC. Figure 10b shows the capacitance retention of the EDLC for 5000 cycles. BXC0.05, BXC0.075 and BXC0.1 are stable at capacitance retention of 93%, 94% and 71.5%, respectively.

Figure 10c, displays the $R_{\text{cap}}$ of the EDLC obtained from complete 5000 charge-discharge cycles. The $R_{\text{cap}}$ for BXC0.025 is from 366 to 646 $\Omega$. This tallies with BXC0.025 leaf-like shape CV plot and large $V_d$. As 0.05 g of MWCNT is included into BC matrix, lower $R_{\text{cap}}$ value can be seen at average of 111 $\Omega$. Meanwhile the values of $R_{\text{cap}}$ for BXC0.075 and BXC0.1 throughout the whole charge-discharge measurement are almost identical. BXC0.1 possesses more stable $R_{\text{cap}}$ value at cycle number of 1500–3000 than BXC0.075 portraying that BXC0.1 has better cation and anion adsorption. Instability or increment of $R_{\text{cap}}$ value is the indicator of ion triplets/pairs/aggregates formation during rapid charge-discharge process [57].

$P_d$ is a measure of how rapidly the energy can be delivered to the external devices which can be seen in Figure 10d. The maximum $P_d$ achieved is 300 W kg$^{-1}$ for BXC0.1. The $R_{\text{cap}}$ is highly related to the $P_d$ of an EDLC. Ions are stripped off/desorp from the surface of BXC during discharge, thus, it is safe to have an EDLC with low internal resistance for better power delivery. The $P_d$ of BXC0.1, BXC0.075 and BXC0.05 undergo some reduction until 1500th cycle before it stabilized until 5000th cycle. The decrement in $P_d$ is due to the development of ionic recombination process during rapid charging and discharging process [58]. The average $P_d$ value of BXC0.025 is 27.9 W kg$^{-1}$. From this, it is safe to say that power density is highly related to the internal resistance especially the gap between electrodes and electrolytes.

$E_d$ is how much energy can be stored in a system. In the case of EDLC, energy is stored in form of electrical double layer. Figure 10e shows the $E_d$ of BXC EDLC at current density of 0.75 mA cm$^{-2}$. The pattern of $E_d$ is almost similar with the trend of $C_i$ in Figure 10a. By referring Eq. (5), $E_d$ is influenced by the specific capacitance. The highest $E_d$ obtained in this work is 1.6 W h kg$^{-1}$ when 0.1 g MWCNT is added. At The electrical properties of the electrode is better at higher concentration of MWCNT. All EDLCs are observed to have a stable value of $E_d$ up until 5000 cycles. The stability in energy density plot means that most ions experienced similar energy barrier during migration process from one BXC electrode to another.

### 3.3.3. Verification of the electrode and electrolyte materials

As we can see in the EDLC section, BXC0.1 has the best performance compared to other electrode compositions. Hence, EIS is done for every BXC electrodes to confirm the trend of EDLC parameters. This can be achieved by monitoring the changes of resistance of the electrodes as MWCNT amount changes. The semicircle in the high frequency region of the Nyquist plot is due to the charge-transfer process [59]. Figure 11 shows that all BXC electrodes possess semicircle. BXC0.025 has electron transfer resistance of 1000 Ohm which is the largest among other electrodes. By referring to Figure 8, it can be observed that BXC0.025 has the

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**Figure 11.** Nyquist plot of each BXC electrodes.

**Figure 12.** Dielectric constants of CS-NaI-Gly before and after charge-discharge process.
biggest voltage drop, meanwhile, BXC0.05, and BXC 0.075 and BXC0.1 electron transfer resistance of 660, 620 and 500 Ohm, respectively. Deng et al. [23] reported an EDLC with MWCNT-cellulose acetate combination. The authors stated that the addition of MWCNT improves the electrical conductivity. Results from Figure 11 are harmonized with the EDLC performance.

Dielectric analysis has been done on CS-NaI-Gly electrolyte which was used in the EDLC after 5000 cycles. BXC0.1 was chosen for this analysis. Dielectric constant (ε) is the stored charge which can be obtained using the following equation:

$$\varepsilon = \frac{Z_r}{\omega C_0 (Z'_r + Z''_r)}$$  \hspace{1cm} (8)

here ω stands for radial frequency while Zr and Zl are the real and imaginary part of impedance, respectively. C0 is the capacitance in vacuum condition. Figure 12 illustrates the ε of CS-NaI-Gly electrolyte after and before charge discharge process. Both plots have higher value at low frequency than at high frequency. At low frequency ions can form a proper charge-double layer at the surface of the electrodes [60]. Apart from that, the value of ε at all frequency for before charge-discharge is slightly higher than after charge-discharge. The reduction of ε signifies the reduction of free ions due to ionic recombination/aggregation in the electrolyte thus leading to a lower charge double-layer. By referring to Figure 10a, C0 of BXC0.1 is higher at the 1st cycle compared to 5000th cycle. Hence, this outcome is harmonized with the charge-discharge analysis.

4. Conclusion

A green, free standing and biodegradable electrode for EDLC based on bacterial cellulose (BC)-multiwalled carbon nanotube (MWCNT) was successfully prepared with a simple and safe technique. These MWCNT-BC electrodes were used to sandwich chitosan (CS)-sodium iodide (NaI)-glycerol (Gly) electrolyte to form an EDLC. The prepared CS-NaI-Gly has high ionic conductivity, transference number and decompose voltage of (1.20 ± 0.26) × 10−3 S cm−2, 0.99 and 2.5 V, respectively, making it useful for the EDLC application design. From XRD analysis, MWCNT-BC electrode possessed the suppressed version of both BC and MWCNT. FESEM analysis revealed that BC has a random web-like network where MWCNT was observed to be well dispersed in between BC network. From CV analysis, no intensity redox peaks are observed thus verifying the capacitive behavior of the fabricated EDLC. From CV also, it was found that, EDLC with high MWCNT amount showed higher specific capacitance than the one with low MWCNT. EDLC with 0.1 g MWCNT possessed the best EDLC performances. Further improvement can be made on the electrodes as well as the electrolyte, such as the addition of nano-filler, polymer grafting, using different types for carbon, salt and polymers. The key is to obtained a really tight contact between the electrodes and the electrolytes.

Declarations

Author contribution statement

Muhammad Hafiz bin Hamsan: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.
Norhana Abdul Halim, Siti Zulakika Ngah Demon: Conceived and designed the experiments.
Nurul Syahirah Nasuha Sa’aya, Norsaadah Ahmad Poad, Norul Farhana Abu Kasim, Nur Amira Mamat Razali: Performed the experiments.
Mohd Fakhrul Zamani Kadir, Zul Hazrin Zainal Abidin, Shujahadeen B. Aziz, Khairel Amali Ahmad, Azizi Miskon, Norazman Mohamad Nor: Contributed reagents, materials, analysis tools or data.

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Data availability statement

The data that has been used is confidential.

Declaration of interest’s statement

The authors declare the following conflict of interests: Norhana binti Abdul Halim reports financial support was provided by Universiti Pertahanan Nasional Malaysia. Halim has. NA Halim has patent Flexible Conductive Composite Sheet and Method Thereof pending to Universiti Pertahanan Nasional Malaysia. NA Halim has patent Flexible EDLC assembled from modified bacterial cellulose pending to Universiti Pertahanan Nasional Malaysia.

Additional information

No additional information is available for this paper.

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