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Lightweight and Flexible Solid-State EDLC based on Optimized CMC-NH_4NO_3 Solid Bio-Polymer Electrolyte

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Supercapacitors attract great interest among researchers as energy storage devices due to their high power capability and long cycle life. In this research, the electrochemical performance of electrical double layer capacitor (EDLC) based solid bio-polymer electrolyte (SBE) was studied. SBE consists of carboxymethyl cellulose (CMC) and ammonium nitrate (NH_4NO_3) was prepared by solution casting technique. The electrical impedance spectroscopy was used to verify the conductivity of SBE. The average conductivity was achieved at $\sim 10^{-3}$ S/cm. This research aims to prepare SBE and apply in the fabrication of EDLC. Scanning electron microscopy analysis showed the smooth and homogeneous surface of SBE film without any phase separation, while irregular shape and sizes of particles was found on the surface of electrode. Elemental identification results yielded that all corresponding elements presence in the SBE and electrode. The EDLC performance was characterized using galvanostatic charge-discharge at different constant currents. Charge-discharge studies showed that long discharge time (90 minutes) within 11 cycle was observed at 2μA. The highest specific capacitance of 1.8 F/g was discovered at 4μA. This study showed that EDLC based SBE has a promising potential to be applied in low current applications.

Keywords: EDLC, solid bio-polymer electrolyte, impedance, charge-discharge

I. INTRODUCTION

The depletion of fossil fuels, environmental concerns and consumers demand on modern and high power equipments/gadgets have driven industries and technologies to search for better energy storage systems. Among those different energy storage systems, one of the most promising candidates is electrical double-layer capacitors (EDLCs) due to its significant merits such as higher power density than conventional (dielectric) capacitors, longer cycle life than secondary batteries, large capacitance, maintenance-free and non-toxic materials [1]-[6]. One of the crucial components in EDLC is an electrolyte. Electrolyte used in EDLC generally aqueous, organic, or liquid salts/ionic liquids [7]-[8]. These

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liquid electrolytes have several hurdles such as being leak-prone, self-discharging, corrosive and bulky [2],[9]. Therefore, the utilization of solid bio-polymer electrolyte (SBE) in energy storage system as an alternative to liquid electrolyte may overcome the leakage and safety issues. SBE also has the ability to form thin film, light weight, flexibility and favourable ionic conductivity [10]-[12]. This SBE also can be easily prepared, using natural polymer which is non-toxic/hazardous materials, as well as has low cost of materials and production. Thus, this research aims to apply a high ionic conductivity of CMC-NH_4NO_3 SBE into the development of EDLC and further investigate its electrochemical performance.

II. MATERIALS AND METHODS

A. SBE film preparation and impedance measurement

The SBE film was prepared according to previous work done by Kamarudin and Isa (2013) via solution casting technique using the optimized composition (the highest ionic conductivity) of CMC:NH_4NO_3 (55:45) with a slight modification [13]. In a clean beaker, ~2.0 g of CMC powder (Across Organics; purity >99.9%; average MW = 90,000 and DS = 0.7) and ~1.6 g NH_4NO_3 (SigmaAldrich; purity >99%) were dissolved in 75 ml distilled water at room temperature. Complete dissolution was achieved after several hours stirring at room temperature using magnetic stirrer. The final clear solution was then poured into separate Petri dishes and left to dry in oven at 50°C for several hours to form thin film. The translucent and flexible SBE film was then transferred to a desiccator for further drying prior to sample characterization. In order to obtain the room temperature ionic conductivity of SBE film, impedance measurement was carried out using electrical impedance spectroscopy (EIS), HIOKI 3532-50-LCR Hi-Tester in the frequency range of 50 Hz - 1MHz.

B. EDLC preparation and characterization

The EDLC electrodes were prepared by mixing a weight ratio of 13:2:1 of activated carbon (RP20 purchased from KURARAY Chemical Co. Ltd.), carbon black (Super-P purchased from Magna Value) and poly(vinylidene fluoride) (PVDF purchased from SigmaAldrich) in 50 ml of N-methyl-2-pyrrolidone (NMP purchased from MERCK). The mixture was stirred until homogenous slurry formed. The slurry was doctor-bladed on aluminium foil current collectors. The prepared electrode was then dried at 80 °C in the oven for 30 minutes, and the electrode was pressed up using a calendaring machine to ensure good contact between aluminium foil and electrode. EDLC cell was then fabricated by sandwiching the SBE film between two electrodes and perspex plates were used to hold the EDLC cell. The schematic diagram of the fabricated EDLC cell is shown in Figure 1. The surface morphology and elemental identification of EDLC electrodes were performed using scanning electron microscope/energy dispersive X-ray (SEM/EDX) Hitachi TM3030 Plus tabletop microscope at room temperature. The electrochemical performance of EDLC cell were tested using galvanostatic charge-discharge (GCD) at different constant currents over 100 cycles. GCD was obtained using NEWARE high accuracy battery tester (5V 1mA).

Figure 1. Schematic diagram of lightweight and flexible solid-state EDLC. The EDLC cell is constructed by stacking electrolyte between two carbon-based electrodes. The cell size is 3.0 cm x 2.5 cm and weight ∼0.2 g.

III. RESULTS AND DISCUSSIONS

A. Ionic conductivity analysis

Table 1 lists the value of surface contact area *(A)*, thickness *(t)*, bulk resistance *(R_b)* and ionic conductivity (σ) of SBE film. The room temperature σ was calculated following equation in [9] and revealed to be $\sim 10^{-3}$ S/cm, which is in agreement with the value obtained by [13].

B. SEM/EDX analysis

SEM/EDX analysis was performed to investigate the surface morphology and elemental identification of SBE film and electrode. Surface morphology of SBE and electrode has a significant impact on the electrochemical activity and transport phenomena that determine the cell performance [14]. Figure **??**(a-b) shows the SEM image and corresponding EDX analysis of SBE film. The surface of SBE appears to be smooth and homogeneous without any phase separation indicating that the NH_4NO_3 salt was completely dissolved in the CMC polymer matrix. Figure 2(c-d) and (e-f) show the surface morphology of electrode before and after the calendaring process with the corresponding EDX analysis. The irregular shape and size of particles were observed from the electrode surface before and after the calendaring. The small white scattered particles were originated from the PVDF binder (Figure **??**(c)). After the calendaring process, those particles were disappeared and fully dissolved in the electrode. The surface of the electrode after calendaring was observed to be smooth and flat as compared to before calendaring which exhibited roughness surface. The stirring process using magnetic stirrer un-

Table 1. The value of surface contact area, thickness, bulk resistance and ionic conductivity of SBE film obtained at room temperature.

Reading	*A* *(cm^2)*	*t(cm)*	R_b (Ω)	σ (S/cm)
1	3.41	2.10 x 10^{-2}	9.01 x 10^{-1}	6.84 x 10^{-3}
2	3.41	2.10 x 10^{-2}	9.69 x 10^{-1}	6.36 x 10^{-3}
3	3.41	2.10 x 10^{-2}	9.52 x 10^{-1}	6.47 x 10^{-3}
				Average σ = (6.56 ± 0.02) x 10^{-3}

able to break the particle into a smaller size, thus calendaring technique was used to obtain a smaller size of electrode materials. The calendaring technique uses pressure to crash the bigger particles into smaller particles. Hence, we can see chunky particles become less and smaller particles can be seen in Figure **??**(e). According to Frackowiak Beguin (2001), an efficient charging of electrical double layer requires materials with a high surface area and pores adapted to the size of ions, which is crucial for supercapacitor performance [15]. The smaller particle will improve the ion absorption in electrode due to the high surface area and high porosity of electron surface. Figure **??**(b) displays the elements present in SBE film. EDX spectrum shows the four most intense peaks of carbon (C), nitrogen (N), oxygen (O) and sodium (Na) as the main elements in SBE. The peaks for Na and C originated from CMC polymer, while peak for N from NH_4NO_3 salt. Figure **??**(d) and (f) show the presence of elements in electrode before and after calendaring. Both electrodes consist of C, O and fluoride (F) with C as main elements from activated carbon and carbon black.

C. Electrochemical performance

Figure 3(a-c) depicts the typical charge-discharge curves of EDLC cell obtained within 11 cycles at different constant currents of 2μA, 4μA, and 6μA. From the figures, a longer charge-discharge period of 90 minutes within 11 cycles was found at 2μA. The charge-discharge curves at all currents were observed to be nearly linear, thus indicating a good capacitive behavior of EDLC [8]. The sudden voltage drop upon discharge can be related to the internal resistance; resistance due to the electrolyte, current collector and the inter-fluid resistance between the current collector and electrolyte [16]. Using the slope of discharge curve, the specific capacitance of EDLC cell was determined using equation reported by [17].

Figure 4(a-c) depicts the plot of specific capacitance versus cycle number at different currents. From the figure, it was observed that the highest specific capacitance of 1.2 F/g, 1.8 F/g and 1.0 F/g were obtained at 2μA, 4μA and 6μA, respectively. According to Yousefi *et al.* (2013), the decreasing trends of the capacitance indicates that certain parts of the surface of the electrode are inaccessible at high charging/discharging rates due to the diffusion effect of the SBE film within the electrode [18]. The fluctuation of specific capacitance between cycle 4 and 6 at 4 μA can be explained due to the unstable reaction of EDLC within those limited periods.

IV. SUMMARY

In conclusion, a free-standing CMC-NH_4NO_3 SBE film was successfully prepared via solution casting technique and fabricated into EDLC. The average ionic conductivity was achieved at

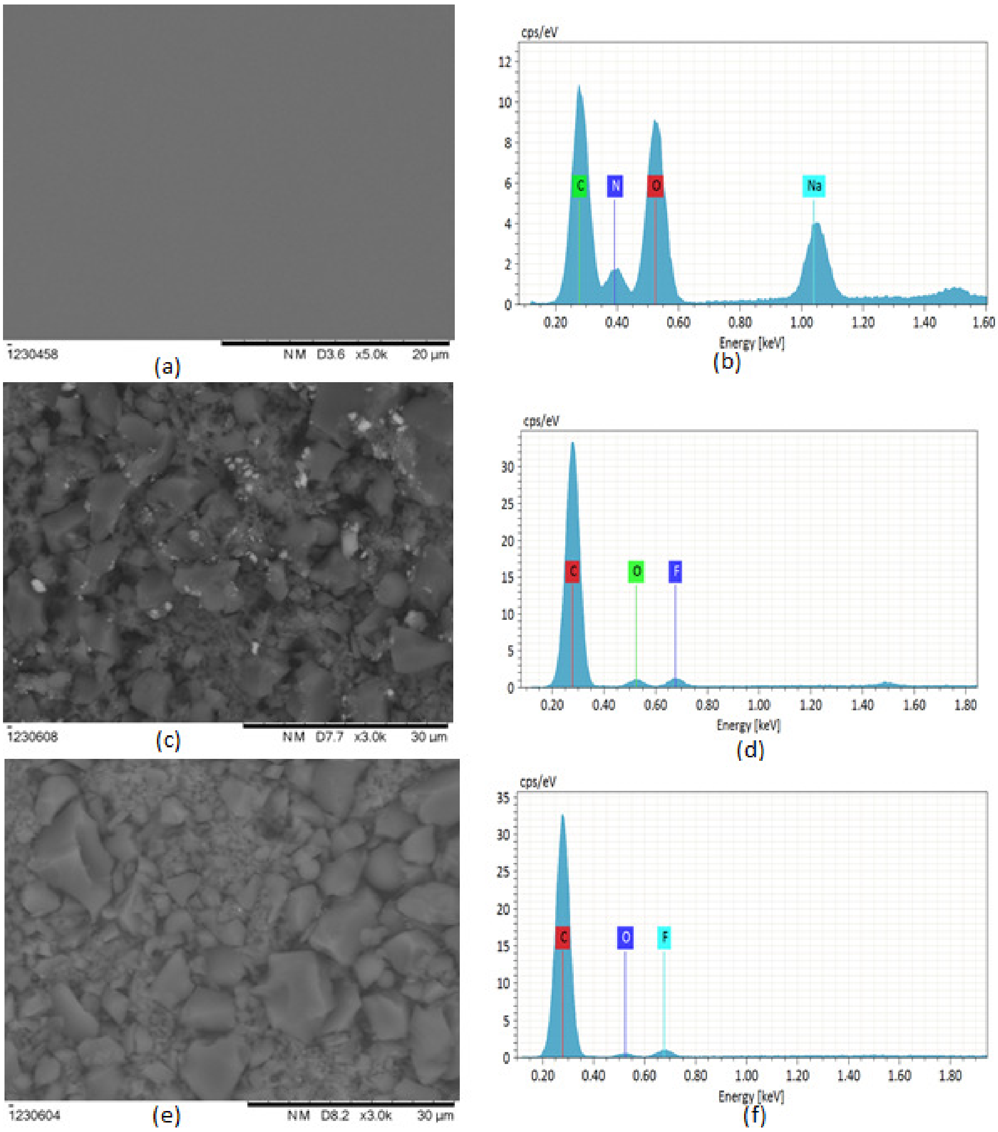

Figure 2. SEM images and EDX analysis of (a-b) SBE film, and EDLC electrode (c-d) before calendaring and (e-f) after calendaring process.

$\sim 10^{-3}$ S/cm. SEM results revealed the surface morphology of electrode and electrolyte. Elemental identification using EDX confirmed the presence of all elements in the electrolyte and electrode. The cyclability analysis at different constant currents in a specific period of time showed the capacitive behavior of EDLC cell. Based on the electrochemical performance, it showed the potential of SBE film to be applied in the EDLC cell for low current application.

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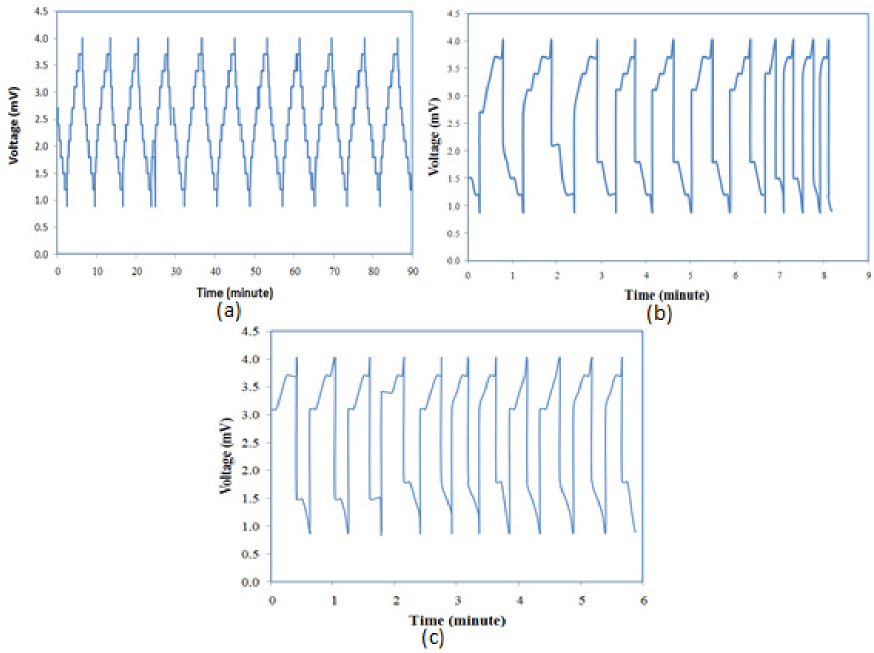

Figure 3. Charge discharge curves within 11 cycles at (a) 2μA, (b) 4μA, and (c) 6μA.

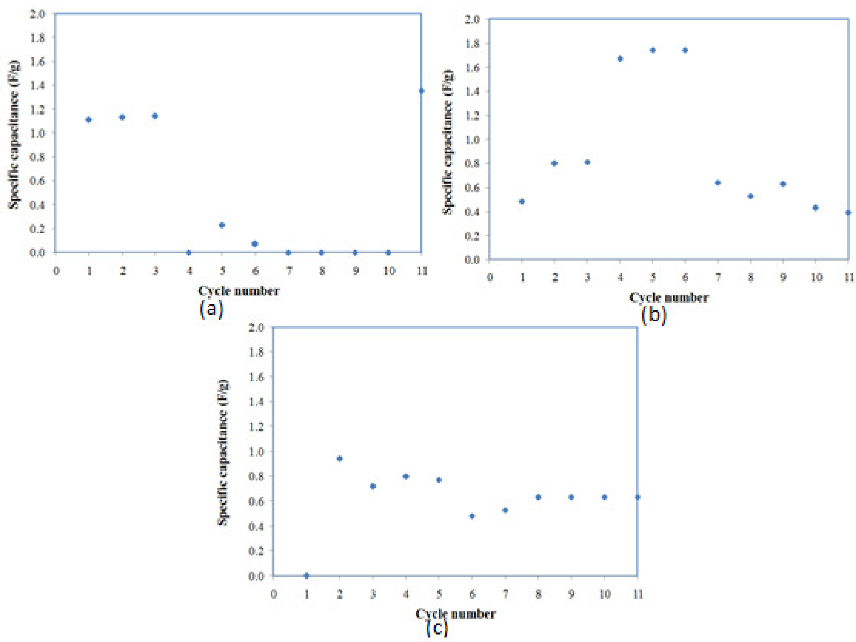

Figure 4. Specific capacitance of EDLC cell within 11 cycles at (a) 2μA, (b) 4μA, and (c) 6μA.

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[1] Xia, L, Yu, L, Hu, Di, Chen, GZ, 2017, Electrolytes for electrochemical energy storage, *Materials Chemistry Frontiers*, vol. 1, pp. 584-618.

[2] A, González, E, Barrena, JA, Mysyk, R, 2016, Review on supercapacitors: Technologies and materials, *Renewable and Sustainable Energy Reviews*, vol. 58, pp. 1189-1206.

[3] Peng, H, Ma, G, Ying, W, Wang, A, Huang, H, Lei, Z, 2012, In situ synthesis of polyaniline/sodium carboxymethyl cellulose nanorods for high-performance redox supercapacitors, *Journal of Power Sources*, vol. 211, pp. 40-45.

[4] Yang, P, Mai, W, 2014, Flexible Solid-State Electrochemical Supercapacitors, *Nano Energy*, vol. 46, pp. 274-290.

[5] Dubal, DP, Kim, JG, Kim, Y, Holze, R, Lokhande, CD, Kim, WB, 2014, Supercapacitors based on flexible substrates: An overview, *Energy Technology*, vol. 2, pp.325-341.

[6] Peng, H, 2015, Fiber-shaped supercapacitor *fiber-shaped energy harvesting and storage devices*, Berlin, Heidelberg: Springer, pp. 117-145.

[7] Yang, H, Yang, J, Bo, Z, Chen, X, Shuai, X, Kong, J, Cen, K, 2017, Kinetic-dominated charging mechanism within representative aqueous electrolyte-based electric double-layer capacitors, *The Journal of Physical Chemistry Letters*, vol. 8, pp. 3703-3710.

[8] Pandey, GP, Kumar, Y, Hashmi, SA, 2010, Ionic liquid incorporated polymer electrolytes for supercapacitor application, *Indian Journal of Chemistry*, vol. 49A, pp. 743-751.

[9] Teoh, KH, Lim, C-S, Liew, C-W, Ramesh, S, Ramesh, S, 2015, Electric double-layer capacitors with corn starch-based biopolymer electrolytes incorporating silica as filler, *Ionics*, vol. 21, pp. 2061-2068.

[10] Hamsan, MH, Shukur, MF, Kadir, MFZ, 2017, NH_4NO_3 as charge carrier contributor in glycerolized potato starch-methyl cellulose blend-based polymer electrolyte and the application in electrochemical double-layer capacitor, *Ionics*, vol. 23, 3429-3453.

[11] Wu, L, Li, R, Guo, J, Zhou, C, Zhang, W, Wang, C, Liu, J, 2013, Flexible solid-state symmetric supercapacitors based on MnO_2 nanofilms with high rate capability and long cyclability, *AIP Advances*, vol. 3, pp. 082129.

[12] Gao, K, Shao, Z, Li, J, Wang, X, Peng, X, Wang, W, Wang, F, 2013, Cellulose nanofiber-graphene all solid-state flexible supercapacitors, *Journal of Materials Chemistry* A, vol. 1, pp. 63-67.

[13] Kamarudin, KH, Isa, MIN, 2013, Structural and dc ionic conductivity studies of carboxy methylcellulose doped with ammonium nitrate as solid polymer electrolytes, *International Journal of Physical Sciences*, vol. 8, 1581-1587.

[14] Aziz, SB, Abidin, ZHZ, 2013, Electrical conduction mechanism in solid polymer electrolytes: New Concepts to Arrhenius equation, *Journal of Soft Matter*, vol. 2013, pp. 1-8.

[15] Frackowiak, E, Beguin, F, 2001, Carbon, *fuel technologies*, vol. 39, pp. 937.

[16] Arof, AK, Kufian, MZ, Syukur, MF, Aziz, MF, Abdelrahman, AE, Majid, SR, 2012, Electrical double layer capacitor using poly(methyl methacrylate)C_4BO_8Li gel polymer electrolyte and carbonaceous material from shells of mata kucing (Dimocarpus longan) fruit, *Electrochimica Acta*, vol. 74, pp. 39-45.

[17] Lim, C-S, Teoh, KH, Liew, C-W, Ramesh, S, 2014, Electric double layer capacitor based on activated carbon electrode and biodegradable composite polymer electrolyte,*Ionics*, vol. 20, pp. 251-258.

[18] Yousefi, T, Daverkhah, Golikand, AN, Mashhadizadeh, MH, 2013, Synthesis, characteriza-

tion and supercapacitor studies of manganese (IV) oxide nanowires, *Material Science in Semiconductor Processing*, vol. 16, pp. 868-876.