DOI: https://doi.org/10.61762/pjstvol7iss1art27054

PLATFORM - A Journal of Science & Technology

Received: 11 June 2024, Accepted: 21 June 2024, Published: 28 June 2024, Publisher: UTP Press, Creative Commons: CC BY 4.0

ELECTROCHEMICAL PERFORMANCE OF SUPERCAPACITOR USING PLASTICISED CORN STARCH POLYMER ELECTROLYTE INCORPORATED WITH LITHIUM IODIDE

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ABSTRACT

An electrical double-layer capacitor (EDLC) is a supercapacitor type that offers higher energy density and capacitance than an electrolytic capacitor. EDLC bridges the energy or power gap between the batteries, fuel cells, and dielectric capacitors. Most EDLCs are fabricated using electrolytic solutions, many of which are highly corrosive, leading to heavy, bulky, and leaky devices. This research assembled an EDLC employing a plasticised solid polymer electrolyte based on lithium iodide (LiI) doped corn starch. Glycerol was used as the plasticiser. The fabricated EDLC was characterised using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge-discharge (GCD) techniques. The specific capacitance obtained from EIS was 1.74 F g^{-1}. By analysing the Nyquist plot obtained from EIS, charge transfer resistance (R_{ct}) and equivalent series resistance (ESR) were determined. CV of the EDLC was carried out at various sweep rates. The highest specific capacitance of 4.66 F g^{-1} was obtained at a 50 mV s^{-1} sweep rate. The EDLC was charged and discharged ten times at 1 mA constant current. From GCD, the specific capacitance was found to be in the 4.36 – 5.57 F g^{-1} range. From these results, starch-LiI-glycerol showed potential as a candidate for electrolyte material for energy device applications.

Keywords: *electrolyte, electrical double-layer capacitor, glycerol, lithium iodide, solid polymer, starch, specific capacitance*

INTRODUCTION

Supercapacitors are capacitors with large capacitance values but with low voltage. These devices can be considered a good alternative to lithium-ion batteries due to low maintenance, high efficiency, and long cycle life. Supercapacitors also have higher energy density than traditional dielectric capacitors [1]-[2]. Supercapacitors' high cyclability and high power density make them suitable for various applications, including electric vehicles, cell phones, medical devices, and wireless power tools [2]. The two main categories of supercapacitors are electrical double layer capacitors (EDLC) and pseudocapacitors. An EDLC comprises electrodes based on carbon of high surface area in which the energy is stored through the non-faradaic accumulation of charges at the electrolyte–electrode interfaces [3]. In pseudocapacitors, conducting polymer or transition metal oxide-based electrodes are used. When voltage is applied, reversible redox reactions occur at the electrode surface, thus storing the energy [4]-[5]. However, pseudocapacitors suffer from the following issues: (i) poor conductivity of active materials, (ii) low power characteristics, and (iii) poor charge-discharge stability [6]. Thus, in this work, the main focus is on the characterisation of EDLC.

Various materials have been employed to serve as electrodes for supercapacitor applications, including graphite, activated carbon, carbon aerogel, and manganese oxide (MnO_2) [7]-[10]. However, activated carbon is preferable owing to its remarkable surface area, conductivity, and electrochemical stability. Parulekar et al. [11] reported that the specific surface area and pore structure of RP20-activated carbon

could directly influence the capacitance of the EDLC, enabling a more significant energy storage capability. The rough structure of activated carbon leads to an increase in internal resistance, thus requiring conductive additives. Carbon black is widely used as a conductive additive due to its good electrical conductivity, high specific surface area, and excellent mechanical and chemical stability [12]-[13]. The binder is another main component of an electrode as it holds the active material together and improves the adhesion between the active material and the current collector [14]. Poly(vinylidene fluoride) PVDF is widely used as a binder for supercapacitor applications due to their ability to show piezoelectric properties, non-toxicity, and thermal, chemical, and mechanical stability [14].

All solid-state EDLC is required to overcome the safety issue associated with electrolyte leakage and reduce the overall volume of cells [15]. The significant challenges in fabricating a solid-state EDLC are developing a high-conducting solid electrolyte and maintaining good charge-discharge stability. Solid polymer electrolytes have been studied since Wright [16] discovered ion-conducting polyethylene oxide (PEO). To our knowledge, there are no reports on applying polymer electrolytes based on corn starch doped with lithium iodide (LiI) and plasticised with glycerol in EDLC. In our previous report, starch:LiI: glycerol at a weight ratio of 49:21:30 achieved the highest room temperature conductivity of $(9.56 \pm 1.19) \times 10^{-4}$ S cm^{-1} [17]. This work reports results from the characterisation of an EDLC employing the starch-LiI-glycerol electrolyte.

METHODOLOGY

Materials

Corn starch, lithium iodide (~99.9% trace metals basis), glycerol (≥99.5%), N-methyl-pyrrolidone (NMP), PVDF, carbon black, and activated carbon were procured from Sigma-Aldrich.

Samples preparation

The preparation of starch-LiI-glycerol electrolyte and carbon-based electrodes was reported in Shukur et al. [17] and Shamsuri et al. [18], respectively. Figure 1 displays the physical appearance of the electrolyte sample.

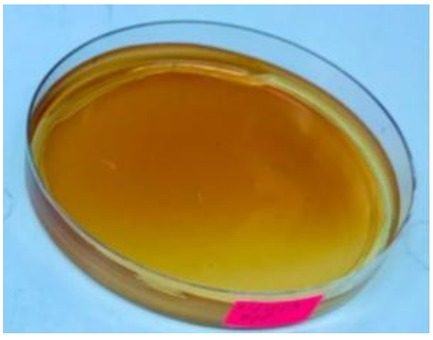
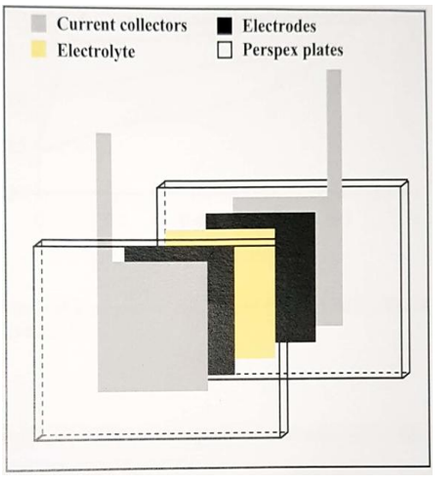


Figure 1 Starch-LiI-glycerol electrolyte

Fabrication and characterisation of EDLC

Starch-LiI-glycerol was placed between two carbon-based electrodes and clamped between two Perspex plates, as shown in Figure 2.

(a)



(b)

Figure 2 (a) Fabrication of EDLC (b) Schematic diagram of EDLC assembly [10]

The electrochemical performance of the fabricated device was investigated employing three different techniques. Impedance spectroscopy was done in a frequency range of 0.01 to 100000 Hz. Cyclic voltammetry (CV) tests were conducted at various sweep rates in the 0 to 1.0 V voltage range. The charge-discharge performance was tested at a constant current of 1 mA between 0 to 1.0 V. All characterisations were done using Metrohm Autolab at ambient temperature.

RESULTS AND DISCUSSION

EIS Analysis

EIS characterisation is a renowned method to assess the electrochemical characteristics of EDLC, including the charge transfer resistance (R_{ct}), equivalent series resistance (ESR), and specific capacitance (C_s). Figure 3 shows the Nyquist plot of the present EDLC. The low-frequency region consists of a tilted spike, which can be assigned to the capacitive behaviour of the device as charge carriers accumulate at the electrolyte-electrode interfaces [19]. At a high-frequency region, an incomplete semicircle curve can be observed. The appearance of this semicircle curve can be ascribed to the double-layer capacitance acting in parallel with charge-transfer resistance [20]. The resistances cause ESR due to the electrodes, the electrolytes, and the contact between the active material and the current collector [18]. ESR can be determined by extrapolating the left side of the semicircular curve to the real axis. The intercept of the curve with the real axis at high frequency represents the ESR. The R_{ct} is attributed to the interfacial resistance obtained by the inhomogeneity at the electrolyte-electrode interfaces [21]. The R_{ct} can be determined by measuring the diameter of the semicircular curve. In the present work, the R_{ct} and ESR are 13 Ω and 12 Ω, respectively. The C_s of EDLC was calculated by using Equation 1:

$$C_s = \frac{1}{\omega_{lowest} Z_{imaginary} M} \quad (1)$$

where ω_{lowest} is the lowest angular frequency, $Z_{imaginary}$ is the imaginary impedance at 0.01 Hz, and M is the mass of active material in both electrodes. The C_s obtained from EIS were found to be 1.74 F g^{-1}.

CV Analysis

The performance of EDLC was further analysed using the CV method at 50, 100, and 200 mV s^{-1} sweep rates, as depicted in Figure 4. No peaks can be observed at all sweep rates, indicating no redox reactions have occurred [22]. This is an expected result as the energy storage in a typical EDLC is a non-faradaic process, i.e., it is achieved via the accumulation of charges at the electrode-electrolyte interfaces. The C_s at different sweep rates was determined using Equation 2:

$$C_s = \frac{1}{(V_1 - V_2) M v} \int_{V_i}^{V_f} I(V) dV \quad (2)$$

where $\int I(V)\, dV$ is the area of the CV plot, $(V_2 - V_1)$ is the voltage range, and v is the sweep rate. Table 1 lists the

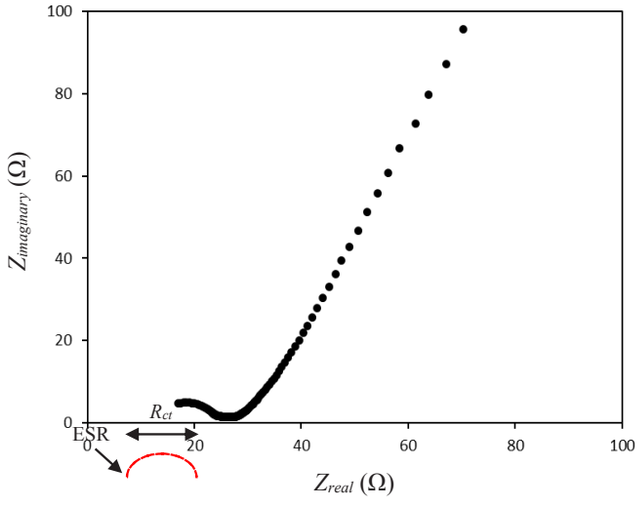


Figure 3 Nyquist plot of EDLC in the frequency range of 10 MHz to 100 kHz

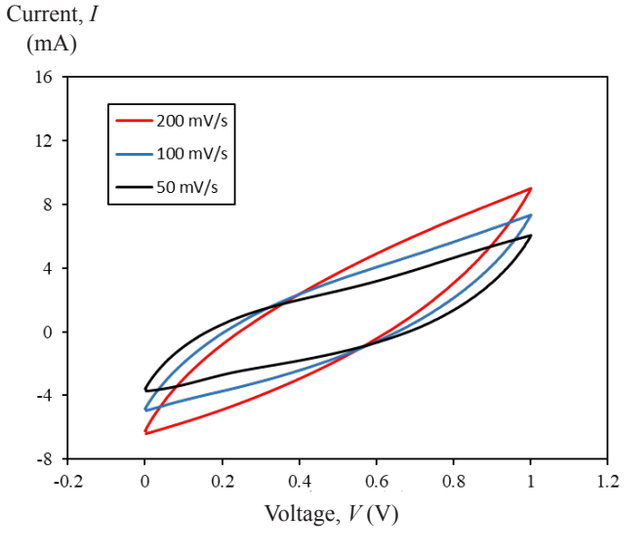


Figure 4 CV plot of EDLC at different sweep rates

C_s at different sweep rates. The lowest C_s of 18.24 F g^{-1} were obtained at 200 mV $s^{-1,}$ while the highest C_s of 46.12 F g^{-1} was obtained at 5 mV s^{-1}. The increase in C_s with a decreasing sweep rate can be attributed to the increase in charge carriers accumulated at the electrode-electrolyte interfaces. At a slow sweep rate, sufficient time was provided for the charge carriers to diffuse into the active electrode material, thus reducing the energy loss [23].

Table 1 The C_s of EDLC at different sweep rates

Sweep rates (mV s^{-1})	C_s (F g^{-1})
50	4.66
100	2.98
200	1.86

Galvanostatic Charge–Discharge (GCD) Analysis

The EDLC was charged and discharged for ten cycles at room temperature. Figure 5 shows examples of the charge-discharge plot of the present EDLC. Voltage drop can be observed prior to the discharging process. This phenomenon is attributable to the ESR. The C_s from the GCD was calculated using Equation 3:

$$C_s = \frac{2I}{M}\left(\frac{\int_{t_i}^{t_f} V(t)dT}{V^2\Big|_{V_i}^{V_f}}\right) \quad (3)$$

where I is the discharge current, V is the voltage range, V_f is the final potential, V_i is the initial potential, and $\int_{t_i}^{t_f} V(t)dT$ is the area under the discharge curve. Figure 6 shows the C_s values for ten cycles. The C_s is almost constant at ~ 5.17 F g^{-1} for ten cycles. The long cyclability with constant capacitance is one of the criteria of a good EDLC.

Electrolyte conductivity significantly influences *Cs*, as reported in the literature [24]-[27]. The conductivity of the present electrolyte was reported to be in order ~ 10^{-4} S cm^{-1} [17]. The C_s obtained in this work are comparable with that of EDLCs using activated carbon electrodes and other solid polymer electrolytes ($\sigma \leq 10^{-4}$ S cm^{-1}), as shown in Table 2.

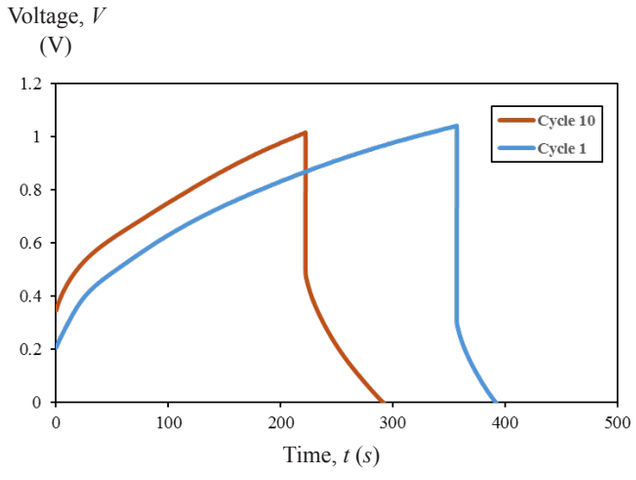


Figure 5 Cycle 1 and Cycle 10 of charge-discharge

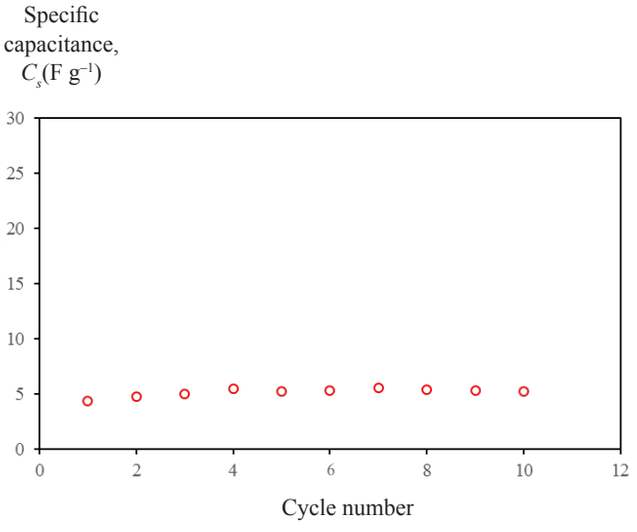


Figure 6 Specific capacitance of EDLC for ten cycles

Table 2 Comparison of C_s obtained from GCD measurement of the present EDLC with other reports

Electrolytes	Conductivity, σ (S cm^{-1})	C_s (F g^{-1})	References
Methylcellulose-NH_4NO_3	2.10×10^{-6}	1.67	[28]
Chitosan-H_3PO_4-Al_2SiO_5	$(1.12 \pm 0.18) \times 10^{-4}$	0.216 – 0.220	[27]
Chitosan-H_3PO_4-NH_4NO_3-Al_2SiO_5	$(1.82 \pm 0.10) \times 10^{-4}$	0.22 – 0.25	[27]
Starch-chitosan-NH_4Cl-glycerol	$(5.11 \pm 1.60) \times 10^{-4}$	~ 3.44	[29]
Starch-LiI-glycerol	$(9.56 \pm 1.19) \times 10^{-4}$	4.36 – 5.57	Present work

CONCLUSION

The present study successfully prepared a starch-based solid polymer electrolyte incorporated with LiI and plasticised with glycerol using a solution casting technique. An EDLC was assembled by sandwiching the electrolyte with carbon-based electrodes. The characteristics of the EDLC were analysed using EIS, CV, and GCS methods. The C_s calculated from EIS was 1.74 F g^{-1}, while the highest C_s obtained from CV was 4.66 F g^{-1} at 50 mV s^{-1} sweep rate. The EDLC was charged and discharged ten times, with the C_s almost constant at ~5.17 F g^{-1}. It was found that the C_s obtained from the three measurements are different. The C_s obtained from EIS depended on frequency and time. CV analysed the C_s by measuring current against fixed potential window and scan rates. In the case of GCD, the C_s were calculated by measuring time against fixed potential and current. The present results show that the starch-LiI-glycerol can potentially serve as electrolyte material for EDLC application development. However, there is still room for improvement. The starch-LiI-glycerol system could be incorporated with nanosized fillers such as titanium dioxide (TiO_2) to improve specific capacitance further. While combining numerous materials can obtain positive outcomes, they can pose some challenges regarding reproducibility and consistency, thus limiting the scalability of these solid polymer electrolytes for large-scale applications. Overcoming these challenges requires interdisciplinary collaboration and careful optimisation.

ACKNOWLEDGEMENT

The author acknowledges the Centre of Innovative Nanostructure and Nanodevices (COINN), Universiti Teknologi PETRONAS (UTP) for providing research facilities.

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