Bentonite Clay Liquid Crystals for High-Performance Supercapacitors

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Abstract
As the human population increases, there is invariably excessive demand for energy sources, thus making it a fundamental need. The basic use of supercapacitors is the storage of energy. But self-discharge is caused when no external power or internal battery is charging them. This clearly reduces their efficiency. It has been found that self-discharge can be reduced to a great extent by employing liquid crystals (LC). But the effect of LC in enhancing the supercapacitor properties has not been discussed. So here, the naturally available bentonite clay is analyzed for its lyotropic liquid crystalline (LLC) properties. It showed liquid crystalline properties at 0.055 g/cm³ in 0.2 M Na₂SO₄ solvent. It is characterized by a polarised optical microscope (POM). These LCs are added as an additive electrolyte to the supercapacitors. The electrode materials used for supercapacitors are a composite of activated carbon and polyaniline. When compared, the supercapacitor properties were enhanced with a decrease in IR drop in supercapacitors containing bentonite lyotropic liquid crystal, producing a specific capacitance of 237.5 F/g at a current density of 0.5 mA/cm². The electrochemical behavior of the supercapacitors is determined by cyclic voltammetry, electrochemical impedance spectroscopy, and galvanostatic charge-discharge cycling techniques.
Introduction

Supercapacitors are the next-generation energy storage device. Their main aim is to reconcile the seemingly incompatible conventional capacitor, which has high power density, and rechargeable batteries, which have high energy density, thus bridging the gap. In the present world situation, renewable energy storage devices are of great demand, in terms of energy security of the nations, transportation, telecommunication and the inevitable climate change. In this context, supercapacitors have a significant role as they can store a large amount of charges between two electrode plates with minimum distance, thus paving a path to miniature and portable energy storage devices. Based on the storage principle, they are of two main types: electric double layer capacitors (EDLC) and pseudocapacitors. In EDLC, charges are stored due to the electrostatic forces (physical forces) observed between the electrodes and the electrolyte due to the generation of a Helmholtz electrical double layer. Here, no new chemical bonds are formed. These supercapacitors usually incorporate carbon-based electrode materials as the active electrode material. In pseudocapacitors, the charges are stored as a result of the actual transfer of electrons or charges between electrode and electrolyte (redox reactions). They are usually made from transition metal oxides or conducting polymer. Thus, the combination of EDLC and pseudocapacitor forms a hybrid capacitor, which can be of three different types: (1) composites, where electrodes have carbon derivatives along with conducting polymer or metal oxides; (2) asymmetric, where one electrode is an EDLC electrode, and the other electrode is a faradic electrode; (3) battery-like, where a supercapacitor electrode is coupled with a battery-type electrode. All these classifications are compiled together as the Taxonomy of Supercapacitors. Metal oxides along with other inorganic compounds can exhibit pseudocapacitance along with electrically operated hydrogen production. Carbon-based symmetric micro-supercapacitors have been reported with greater specific capacitance, cyclic stability, specific energy using conventional organic binders and separators. Highly efficient self-healing polyelectrodes with high flexibility, mechanical endurance and electrochemical character using SWCNTs are also available. Some studies employing the biological chitosan and CNT nanocomposite as electrode material were also investigated, which led to the enhancement of supercapacitors.
Liquid crystals are a state of matter that have properties linking traditional isotropic liquids and crystalline solids. They have liquid-like fluidity and solid-like orientation. Thus, based on physicochemical parameters, there are two main types: thermotropic, where the thermal process is responsible for transformation into the mesophase, and lyotropic, where the main constituent is the amphiphilic molecules which have a polar head and non-polar tail. These lyotropic liquid crystals (LLC) are capable of forming self-assembled systems, micelles, at a particular concentration in a suitable solvent. This is considered their critical micelle concentration (CMC). Thus, if the concentration of the amphiphilic molecules is equal to CMC, micelle formation enhances. There is direct and indirect polymorphism in LLC. In a polar solvent, the non-polar chains are squeezed into the inner region, and the polar head forms the outer region, forming direct polymorphism. In a non-polar solvent, the polar head is confined in a closed region and the non-polar tail is exposed to the external solvent medium, leading to inverted polymorphism.15

Bentonite clay is an aluminum phyllosilicate absorbent-swelling clay. These bentonite clays are framed of two structural sheets in a T-O-T fashion, i.e., they have two tetrahedral silica sheets, which sandwiches a central octahedral aluminum sheet. They form the negative crystal charge, which is stabilized by the exchangeable cations such as Na+, Ca2+, K+. It is these cations that interact with the water molecules through ion-dipole secondary interaction bonds.16 Gabriel, Paineau, and Maiti reported that clay showed liquid crystalline properties.17–19 Gabriel said that bentonite liquid crystals showed nematic lyotropic liquid crystalline properties when observed under POM. Ramos-Tejada investigated the electrorheological response of different clay particle suspensions and claimed that they have sufficient electrorheological response.20 Electrorheological fluid is a suspension with an apparent viscosity that changes to a great extent in response to the electric field. Thus, by regulating the applied electric field, the viscosity of the fluid can be controlled.21

In most of cases in the existing literature where additive electrolyte has been added to enhance the supercapacitor performance, i.e., either by increasing the specific capacitance or decreasing the self-discharge, there was not much change in the electrochemical behavior of the supercapacitors. Additive electrolytes have only a positive impact on reducing self-discharge. Supercapacitors in the charged state are in a high-energy state. Any matter that does not stay in its particular charged state for a long time will tend toward the lower stable energy state. There is a quasi-driving force for material to return to the lower energy state. As it follows, the charged supercapacitors gravitate towards the steady low-energy discharged state. This phenomenon is called ‘self-discharge’, which is one of the main limitations of supercapacitors.22 So different aspects were explored to enhance the supercapacitor performance. Fic in 2010 carried out a comparative work on the effect of three different types of surfactants on the self-discharging phenomena in supercapacitors. The nonionic surfactant TRITON in acidic medium showed only 25% of self-discharge when compared with the pure acidic medium which showed 63% after 20 h at open-circuit voltage.23 Wang in 2014 utilised solvated species of electrolyte to increase voltage retention in supercapacitors by 62%.24 Xia in 2018 employed nematic liquid crystal (LC)—[4-η-pentyl-4’-cyanobiphenyl] (5CB) as an additive electrolyte to arrest the self-discharge of EDLCs to a great extent.25 Also, for EDLCs, lyotropic liquid crystal (LLC) formed by the assembly of co-polymer and an ion liquid is used as an additive electrolyte, which was studied in 2019 by Liu et al.26 Haque in 2020 employed 5CB LLC in Li2SO4 electrolyte which showed 96% voltage retention.27 But here we have achieved an improved supercapacitive nature of the supercapacitor, only by the addition of the naturally abundant and cost-effective bentonite clay. Further studies on the concept of self-discharge can also be conducted. So here, naturally available Bentonite clay, possessing lyotropic liquid crystal properties with electrorheological response, was used to analyze its effect as an additive electrolyte in supercapacitors containing activated carbon-polyaniline composite electrodes.

**Experimental Section**

**Materials Required and Methods**

Commercially available bentonite clay was used for liquid crystalline analysis. Aniline, sulphuric acid, and sodium dodecyl sulphate were procured from Loba Chemie Pvt. Ltd., Mumbai, India. Activated carbon (Darco, — 100 mesh particle size) was purchased from Sigma Aldrich. Commercial 304-grade stainless steel (ss) was used as an electrode substrate. Surfactant-aided electropolymerization of aniline and electrochemical characterization were executed on a Potentiostat (BioLogic SP-150).

**Clay Liquid Crystal Preparation**

To observe the liquid crystalline phase of bentonite clay, the following procedure was used.15 10 w/v of bentonite clay was put into a flask with distilled water of pH 6. The mixture was rigorously stirred for 24 h. The suspension was centrifuged for 6 h. Yellow, slightly homogeneous, exfoliated clay was obtained. Later, by dissolving in various basic pH solutions, the lyotropic liquid crystalline properties were studied under a POM (polarising optical microscope).
Fabrication of Composite Symmetric Supercapacitors

The working electrodes were setup on a stainless-steel sheet (1 cm×1 cm). A homogeneous slurry of activated carbon with 1% binder poly(vinylidene fluoride) (PVdF) was coated uniformly on the stainless steel. It was heated in a vacuum for 5 h. Electrochemical polymerization of aniline was done on the working electrode, using cyclic voltammetry (CV) between 0.8 V and −0.2 V. During this, 0.8 M of sulphuric acid (H₂SO₄) was used as an electrolyte with 0.057 g of surfactant sodium dodecyl sulphate (SDS) was added. The counter electrode platinum and reference electrode calomel were used. The electrode material composite of activated carbon and polyaniline was found to be ~0.001 g. The symmetric supercapacitor was constructed using the composite electrodes, separated by a separator.

Electrochemical Characterization

The supercapacitors were analyzed using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge/discharge (GCD).

Results and Discussion

Clay Liquid Crystal Analysis

For the liquid crystal analysis under POM, the exfoliated clay was dissolved in sodium sulphate (Na₂SO₄) solvent. Critical micelle concentration (CMC) is an important parameter that determines the formation of lyotropic liquid crystals. Concentrated clay suspensions around 0.055 g/cm³ showed the finest type of lyotropic nematic liquid crystal formation in 0.2 M Na₂SO₄ (Fig. 1d) solvents with a direct type of micelle polymorphism. This is the critical micelle concentration because the concentrations of clay suspensions below this CMC were analyzed, but they did not show any recognizable micelle formation. The POM images of those concentrations below the CMC are also shown in Fig. 1a, b, and c. There was no apparent micelle formation. Therefore, the concentration at which the lyotropic nematic phase was observed is taken for the electrochemical investigation of the supercapacitor. All these analyses were performed at room temperature.

Electrochemical Analysis of Symmetrical Supercapacitors in a Two-Electrode Cell

Two symmetric composite electrodes of activated carbon/polyaniline were set up as supercapacitors for further electrochemical analysis. The electrode used here is a 0.2 M Na₂SO₄ solution. The analysis is done by comparing the parameters of the supercapacitors ‘without clay’ (blank) and ‘with clay liquid crystal’ (W-CLC). The clay here is added as the additive electrolyte along with the electrolyte. In Bentonite clay suspension, the colloidal stability is of great importance. The electrical charge of the diffused layer of the colloid and the range of the charge’s impact into the solution are reflected by the zeta potential (ZP). In Na₂SO₄ solutions, when the pH was varied, it showed no effect on the ZP of bentonite clay particles. Also, at different concentrations of Na₂SO₄ solution, bentonite clay did not show any alteration in the surface charge, thus confirming that the Bentonite clay suspensions are stable.

W-CLC supercapacitor was set up on the following basis. We have concluded that 0.055 g/cm³ is the critical micelle concentration of clay, i.e., 0.055 g of clay in 1 cm³ of solvent, showing lyotropic liquid crystal properties at 0.2 M concentration of the solvent. According to the literature, 2 vol.% of additive electrolyte must be used. For 20 cm³

![Fig. 1 POM images observed for 0.055 g of clay in different Na₂SO₄ solvent concentrations. (a) In 0.05 M Na₂SO₄ (b) In 0.1 M Na₂SO₄ (c) In 0.2 M Na₂SO₄, showing lyotropic aggregates with nematic phase; (d) In 0.2 M Na₂SO₄, showing lyotropic nematic micelle formation in the lower right corner.](image-url)
electrolyte, 1.1 g of clay is added. This is the supercapacitor setup with clay.

Cyclic voltammetry shows the current response as a function of the applied potential. For both blank and W-CLC, it was carried out in various scan rates of 2, 5, 10, 20, 50, and 100 mV/s. For all these scan rates, both supercapacitors were swept between an established voltage window of 1 V to −1 V. The results obtained are shown in Table 1. The cyclic voltammogram obtained showed a quasi-rectangular plot along with the redox peaks. This is attributed to the presence of the EDLC and pseudo-capacitance. Here, it is noted that when the scan rate increases, the current density increases with it. This is because, as the scan rate increases, the rate of diffusion increases and thus the current density. The results obtained are shown in Fig. 2.

The value of specific capacitance from CV is calculated by using the formula

\[ C_p = \frac{A}{2 \times m \times K} \]  

(1)

where \( A \) = area under the curve, \( m \) = mass of the electrode material, \( K \) = scan rate.

It is multiplied by 2 because capacitance is formed from the two-electrode setup.

From this, there is a clear improvement in the capacitance values when clay as lyotropic liquid crystal was added as additive electrolyte. The comparison is shown in Fig. 3. This may be because, in the electrolyte, since the clay is an ionic micelle which can undergo cation and anion exchange, \(^{31}\) it facilitates the speeding up of the electrolyte ion movement from the electrolyte to the electrode interface by holding them firmly to the clay micelles through weak van der Waals forces, thus increasing the overall electrochemical reactivity. The movement of the clay micelle can be attributed to its electrorheological property. \(^{20}\) Therefore, in the W-CLC supercapacitor, ionic clay micelles benefit the existing capacitance of EDLC and pseudo-capacitance, which results in a synergistic effect on capacitance. Here, at 10 mV/s, for the blank, the specific capacitance was 101.44 F/g, but for W-CLC, it was four times this value, i.e., 466.37 F/g, exhibiting an evident increase in specific capacitance. Comparison is shown in Fig. 4. Thus, 10 mV/s can be considered optimal for the functioning of the W-CLC supercapacitor. Here, this scan rate might allow the complete diffusion of the entire clay micelle with electrolyte ions, as they have a large surface area leading to high ion-exchange. \(^{31}\) Hence the extent of doping-dedoping will increase. In lower scan rates (2 mV/s and 5 mV/s, which have almost the same SC values), the entire large clay micelle may not undergo complete diffusion.

| Scan rate (mV/s) | Specific capacitance of composite electrodes (F/g) |
|-----------------|--------------------------------------------------|
|                 | Blank    | W-CLC   |
| 2               | 259.7    | 160.67  |
| 5               | 258.44   | 120.44  |
| 10              | 101.04   | 466.37  |
| 20              | 45.78    | 249.05  |
| 50              | 24.8     | 48.21   |
| 100             | 25.184   | 39.13   |

**Fig. 2** Cyclic voltammograms of two supercapacitors (a) without clay (Blank) (b) with clay liquid crystals (W-CLC).

**Fig. 3** Comparison of specific capacitance of blank and W-CLC.
at the interface and thus slowing down the ion-exchange process.

The further analysis of the electrochemical feature of these supercapacitors was achieved by using electrochemical impedance spectroscopy, which establishes the electrochemical reaction mechanisms along with the values of kinetic parameters involved in the mechanism. It basically provides electrical information of the electrolyte, electrode materials, and the interfaces. This approach entails measuring the cell impedance at various temperatures and frequencies and examining the results in a complex impedance plane. Impedance is similar to resistance but varies as it also accounts for the effects of capacitance and inductance. As impedance is frequency-dependent, this technique was studied over a wide frequency range (100 mHz–1 MHz). A Nyquist plot (results shown in Fig. 5) is a mapping of the impedance values in a complex plane. This plot comprises an almost semi-circle in the high-frequency zone and a straight line in the low-frequency zone. It is the ion diffusion, that generates the charge transfer resistance ($R_{ct}$) and Warburg resistance. Charges are continuously being transferred in the solution due to the Faradic reactions. Its speed is dependent on temperature, concentration gradient, potential, and other reaction parameters. $R_{ct}$ is the impedance value corresponding to the semi-circle zone. Warburg resistance is less in the high-frequency zone because the electroactive species diffuse for a short distance, but at low frequency,

![ Nyquist impedance plots of two supercapacitors (a) Blank (b) W-CLC (c) comparison of (a) and (b) (d) Z-fit of Blank (e) Z-fit of W-CLC. ](image-url)

Fig. 4 CV of blank and W-CLC at 10 mV/s.

Fig. 5 Nyquist impedance plots of two supercapacitors (a) Blank (b) W-CLC (c) comparison of (a) and (b) (d) Z-fit of Blank (e) Z-fit of W-CLC.
they diffuse for a longer distance creating high impedance. It takes the form of a diagonal line with a 45° slope.\textsuperscript{30}

For the quantitative comparison of Blank and W-CLC supercapacitors, EIS data are usually analyzed by fitting the obtained plot to an equivalent circuit model. These circuits contain classic electrical elements such as resistors, inductors, and capacitors.\textsuperscript{3,32} This is called Z-fitting. Z-fit values along with the calculated values for the Nyquist plot are given in Table II. When the Nyquist plots of both are compared, it is seen that the Nyquist plot of W-CLC is within the charge transfer range (semicircle) of the Blank’s Nyquist plot. This tells us that the clay micelles assisted in the electrolyte ion movement towards the interface, where it underwent the faradic reaction, which consequently enhanced the capacitance of W-CLC. As the bentonite clay itself possesses electrorheological properties when in the influence of an external electric field, which in turn controls its viscosity, this also validates that addition of an additive electrolyte has no negative effect on the mobility or kinetic parameters of the electrolyte.

From the same results, a Bode plot (Fig. 6) is obtained, complementing the Nyquist plot. The Bode plot consists of two plots combined. The first plot is between impedance versus frequency, and the second plot is between phase angles versus frequency. From this, the time constant (\(\tau_o\)) value can be derived. The time constant of the system determines how fast or slow the system responds. Low \(\tau_o\) means a faster response. The time constant here is the point when supercapacitor transitions from resistive at high frequency to capacitive behaviour at low frequencies. It is calculated as the time constant, \(\tau_o = 1/\log f_o\) when \(\log |Z| = \text{phase}(Z)\).\textsuperscript{30}

The time constant (\(\tau_o\)) which is calculated and from the Z-fit plot is given in Table III. The values of \(\tau_o\) for the Blank and W-CLC supercapacitors are 0.27 s and 0.23 s, respectively.

| Parameters obtained from Nyquist Plot | Solution resistance (Ω) | Charge transfer resistance, \(R_{ct}\) (Ω) | Warburg resistance (Ω) |
|-------------------------------|-------------------------|------------------------------------------|------------------------|
|                               | Calculated value        | Z-fit value                              | Calculated value       | Z-fit value |
| Blank                         | 0                       | 2.685                                    | 73                     | 65.05       | 211.3       | 231.7       |
| W-CLC                         | 2                       | 1.99                                     | 29.3                   | 21.74       | 45.7        | 49.73       |

Fig. 6  Bode plots of two supercapacitors (a) Blank (b) W-CLC (c) Z-fit of Blank (d) Z-fit of W-CLC.
From the smaller time constant of W-CLC, it is inferred that there is very small or no constricted movement of charges during the charge-transfer process, even after the addition of the ionic clay micelles as additive electrolytes.

Galvanostatic charge discharge (GCD) cycling experiments were utilized for the study of electrochemical properties. This is shown in Fig. 7. From this methodology, other parameters such as supercapacitance \( C_s \), specific energy (SE), specific power (SP), IR drop, equivalent series resistance (ESR), coulombic efficiency \( N\% \) were analyzed.\(^\text{30}\)

These are calculated by using the equations

\[
C_s = \frac{2I\Delta t}{\Delta V m}
\]  
(2)

\[
\text{SE (Wh kg}^{-1}\text{)} = \frac{I\Delta V \times 1000}{m \times 3600}
\]  
(3)

| Table III  | Parameters obtained from Bode plot |
|------------|------------------------------------|
|            | Time constant, \( \tau_0 \) (s)    |
|            | Calculated value | Z-fit value |
| Blank      | 0.27 | 0.25 |
| W-CLC      | 0.23 | 0.23 |

![Fig. 7 Charge–discharge curves at different current densities for W-CLC.](image)

Table IV  Parameters obtained from charge–discharge cycles

| Current density (mA/cm\(^2\)) | SC (F/g) | SE (Wh kg\(^{-1}\)) | SP (W kg\(^{-1}\)) | IR drop (V) | ESR (\(\Omega\)) | \(N\%\) |
|-------------------------------|---------|------------------|------------------|-------------|----------------|---------|
| Blank                         | 0.5     | 182.87           | 3.73             | 191.85      | 0.6            | 0.6     | 38.3   |
|                               | 1       | 53.83            | 1.44             | 391.2       | 0.6            | 0.3     | 39.1   |
|                               | 2       | 15.29            | 0.24             | 679.8       | 0.6            | 0.1     | 33.9   |
| W-CLC                         | 0.5     | 237.5            | 20.68            | 395.9       | 0.2            | 0.3     | 79.2   |
|                               | 1       | 234.9            | 12.33            | 614.8       | 0.3            | 0.2     | 61.5   |
|                               | 2       | 126.2            | 7.77             | 1332.4      | 0.3            | 0.08    | 66.6   |

}\( \text{SP (W kg}^{-1}\text{)} = \frac{I\Delta V \times 1000}{m} \)  
(4)

\[
\text{ESR (VA}^{-1}\text{)} = \frac{\text{IR drop}}{2I}
\]  
(5)

\[
N\% = \frac{\text{Discharge potential}}{\text{Charge potential}} \times 100
\]  
(6)

where \( I \) = applied discharge current, \( \Delta t \) = discharge time after IR drop, \( \Delta V \) = discharge potential window after IR drop, \( m \) = mass of single electrode material.

It is multiplied by 2 as two electrodes are used in setting up the supercapacitor.

The values are shown in Table IV.

Here, in GCD, as the current density increases from 0.5 mA/cm\(^2\), 1 mA/cm\(^2\), and 2 mA/cm\(^2\), the charge-discharge time decreased. This is attributed to the electrolyte ions which had ample time to explore the electrode’s vast surface and interior at low current density, resulting in a higher capacitance. But at higher current density, owing to insufficient ion diffusion at the vicinity of the electrode, capacitance decreased, and maybe only the superficial surface of the electrode could be used to accumulate charge.\(^\text{30}\)

Figures 7 and 8 are the results of GCD at different current densities of 0.5 mA/cm\(^2\), 1 mA/cm\(^2\), 2 mA/cm\(^2\). The specific capacitance values obtained at 0.5 mA/cm\(^2\) for Blank and W-CLC supercapacitors are 187.87 F/g and 237.5 F/g, respectively. In the W-CLC supercapacitor, along with the electrolyte ions, the clay ionic micelles which have exchangeable ions, are also involved in exploring the electrode material thoroughly, thus leading to the increase in the charge storing capacity and the specific power of the W-CLC supercapacitor is seen, after including LLC in the electrolyte.\(^\text{26}\)

Decreases in IR drop and ESR are seen in the supercapacitor in the presence of lyotropic liquid crystal which is in accordance with the lower charge-transfer resistance and Warburg resistance of the W-CLC supercapacitor, confirming the free, outspread movement of charges during charging and discharging. The capacitance stability of the W-CLC supercapacitor was
examined and cycling stability curve is shown in Fig. 9. The capacitance retention of 80% at 1000 cycles was found with specific capacitance values 237.5 F/g, 225.6 F/g, 213.75 F/g, 199.5 F/g, 190 F/g at 1st, 250th, 500th, 750th, 1000th cycles. These values continue decreasing because of the continuous doping and de-doping of the conducting polymer backbone during charging/discharging, leading to the deterioration of the polymer gradually. This behaviour depicts the stability of the W-CLC supercapacitors set-up, even after the addition of the additive electrolyte. These electrochemical characterizations can also be conducted on CNTs as the active electrode materials and compared.

Here we have achieved improved the super-capacitive nature of the supercapacitor by the addition of the naturally abundant and cost-effective bentonite clay. The findings presented in this chapter were in accordance with the research literature. The supercapacitors with additive electrolyte data obtained from the literature along with this result are compiled in Table V.

**Conclusion**

In this work, we have demonstrated that the naturally available bentonite clay showed evident nematic liquid crystalline properties at a CMC of 0.055 g/cm$^3$ in 0.2 M Na$_2$SO$_4$ solvents with a direct type of micelle polymorphism. When 2 vol.% of these liquid crystals were added as an additive electrolyte to the supercapacitor setup, they enhanced supercapacitor properties with a specific capacitance of 237.5 F/g at a current density of 0.5 mA/cm$^3$. This enhancement was achieved by using the naturally available entonite clay and hence can be considered as a cost-effective method. Further research on the effect of clay liquid crystals on suppressing self-discharge can be studied.
Table V  Supercapacitors along with additive electrolyte

| Electrode material               | Electrolyte            | Additive electrolyte added | SC (F/g)                | Effect in suppressing self-discharge | References |
|---------------------------------|------------------------|----------------------------|-------------------------|--------------------------------------|------------|
| 1. Commercial carbon black     | 1 M KOH                | Surfactants                | 118 @ 10 A/g            | Voltage retention (%/h) 63/20 h       | 23         |
| (Norit + PVDF + acetylene black) |                        | SDS                        | 145                     |                                      |            |
| (TRITON)                        |                        |                            | @ 10 A/g                |                                      |            |
| 2. Carbon fibre papers          | 0.3 M KI               | Solvated redox-active      | N/M                     | Voltage retention (%/h) 62/12 h       | 24         |
| species 0.2 M VOSO₄             |                        |                            |                         |                                      |            |
| 3. Activated carbon + acetylene black + Carboxymethyl cellulose | TEMABF₄/acetonitrile   | Nematic liquid crystal     | 31 mF @ 0.5 mA          | Voltage retention 71/24 h            | 25         |
|                                 |                        | 2% 5 CB Blank              | 31 mF @ 0.5 mA          |                                      |            |
| 4. Activated carbon + acetylene black + Carboxymethyl cellulose | TEMABF₄/acetonitrile   | 5% triblock liquid crystals | 38 mF @ 0.5 mA          | When compared with blank OCP, decay reduced by 32% and leakage current reduced by 74% | 26         |
|                                 |                        | of triblock copolymer      | 38 mF @ 0.5 mA          |                                      |            |
|                                 |                        | Pluronic 64 & ILs [BMim] Bf₄ | Blank                   |                                      |            |
| 5. activated carbon fabric (ACC 507-20) | 1 M LiSO₄             | Nematic liquid crystal     | 118.7 @ 1 mV/s          | 90/1 h                               | 27         |
|                                 |                        | 2% 5 CB Blank              | 125.4 @ 1 mV/s          |                                      |            |
| 6. Activated carbon + PVDF + polyaniline | 2 M Na₂SO₄         | 2% Nematic clay liquid     | 237.5 @ 0.5 mA/cm³      | Research gap                         |            |
|                                 |                        | crystal                   | 182.87 @ 0.5 mA/cm³     |                                      |            |

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Conflict of interest The authors declare that they have no conflict of interest.

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