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# Redox active bio-ionic liquid electrolyte for high energy density Zn-ion capacitor

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## HIGHLIGHTS

• Redox active bio-ionic liquids are promising electrolytes for Zn-ion capacitors.

- Bio-ionic liquid interaction with graphene enhances the charge storage capability.
- The Redox species in the bio-ionic liquid leads to Faradaic charge storage process.
- The biocompatible Zn ion capacitor shows a good stability for 5000 cycles.

## ABSTRACT

Zinc-ion capacitors are attracting significant interest due to their safety, recyclability, and high theoretical capacity (820 mAh g<sup>-1</sup>). Most studies on Zn-ion capacitors focus on aqueous electrolytes, but these limit the electrochemical window and often lead to dendrite formation. In contrast, aprotic ionic liquid electrolytes extend the electrochemical window but suffer from slow diffusion kinetics of Zn species, which can reduce power density. In this work, we introduce a sustainable and biocompatible redox electrolyte based on bio-ionic liquids (Choline acetate and Choline iodide) for Zn-graphene capacitors. This electrolyte results in a high storage capacity of 350 F g<sup>-1</sup> at a current density of 0.5 A g<sup>-1</sup>. Electrochemical tests, in situ Atomic Force Microscopy (AFM), and Density Functional Theory (DFT) studies reveal that choline in the electrolyte interacts with graphene, altering its local electronic structure and enhancing its capacity. The presence of choline iodide further improves the capacity through a redox reaction on the graphene surface. Stability tests at 3 A g<sup>-1</sup> show an initial capacity of 160 F g<sup>-1</sup>, which decreases to 130 F g<sup>-1</sup> after 5000 cycles, yielding a capacity retention of 81.5 %. This study paves the way for the development of biocompatible hybrid capacitors for a range of applications.

# 1. Introduction

The development of sustainable, high-energy, and high-powerdensity storage systems that are cost-effective is essential for efficiently storing the intermittent energy produced by renewable sources [1]. While batteries are typically favoured for their high energy density, hybrid capacitors offer a more suitable solution for intermittent energy storage, as they combine both high energy and power densities [2]. Among the various hybrid capacitors, Zinc-ion capacitors (ZICs) present a promising, cost-effective alternative due to their safety, ease of recyclability, high theoretical capacity (820 mAh g<sup>-1</sup>), and compatibility with a range of electrolytes [3–5].

However, in aqueous electrolytes, Zn anodes are prone to dendrite

formation at high current densities, along with parasitic reactions such as hydrogen evolution, zincate formation, and reduced coulombic efficiency [6]. These issues also arise in aprotic ionic liquid electrolytes [7]. Consequently, modifications to the Zn anode are often required, which can introduce additional side reactions [8]. Altering the Zn solvation structure within the electrolyte has shown to mitigate dendrite formation and improve the stability of ZICs [8–10]. The solvation structure can be influenced by the choice of electrolyte (aqueous, organic, or ionic liquids) and the specific anion composition [8], making electrolyte selection a critical factor in the development of high-energy and high-power ZICs.

Recently, redox-active electrolytes have emerged as a promising approach to enhance the energy density of capacitors [11-23]. The

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increased energy density is attributed to the combined contribution of capacitive and faradaic processes involving redox-active species. In aqueous electrolytes, the inclusion of redox species such as iodide, hydroquinone, or VOSO4 has been shown to increase energy density. However, due to solubility limitations, the enhancement in energy density is often modest, and self-discharge remains a significant issue [11,15,16]. In aprotic ionic liquids, the addition of redox-active species, such as 1-ethyl-3-methylimidazolium iodide (EmimI), improves the double-layer capacitance, though substantial capacity fading is observed over time [14]. Recent work by Mourad et al. [12,17] demonstrated that bi-redox ionic liquids containing anthraquinone and 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) as moieties, attached to perfluorosulfonate anions and imidazolium cations, can provide a two-fold increase in capacitance ( $\sim$ 150 F g<sup>-1</sup>) on reduced graphene oxide (rGO) compared to systems without these bi-redox ionic liquids. Khakani et al. showed that adding a redox moiety in ionic liquids can improve the stability of batteries [19]. Despite these improvements, challenges related to cost, toxicity, and recyclability persist with redox-active aprotic ionic liquids. Moreover, energy density was typically evaluated at low current densities  $(0.1 \text{ A g}^{-1})$  [22], limiting the practical applicability of these systems. Some studies have also employed toxic selenium-based cathodes, further restricting the scalability and environmental sustainability of the technology [23].

In this work, we present a sustainable and biocompatible Zngraphene capacitor that achieves both high energy and power densities, facilitated by a redox-active bio-ionic liquid electrolyte composed of Choline acetate (ChAc) and Choline iodide (ChI). Through a combination of electrochemical characterization, in situ techniques, and Density Functional Theory (DFT) calculations, we demonstrate that Choline interacts with the graphene surface, leading to enhanced energy storage. Furthermore, the addition of ChI facilitates a redox reaction on the graphene surface, further boosting the capacitor's energy storage performance.

#### 2. Experimental

Choline acetate (95 %) was purchased from Iolitec. Choline Iodide (98 %) and Zn acetate (99.99 %) were purchased from Fisher Scientific. Zn (99.9 %) was purchased from Pi-Kem and graphite paper was purchased from RS Pro. Graphene was purchased from Nanographi. The electrolytes were prepared by mixing various concentrations of Zn acetate/Choline acetate/choline iodide in distilled water and stirred at room temperature for 2 h before use.

Electrochemical measurements were carried out in a split cell consisting of graphene coated graphite paper as the working electrode, Zn foil as counter and reference electrodes with different electrolytes. CV was performed in the potential range of 0–1.8 V vs Zn at different scan rates from 5 to 200 mV s<sup>-1</sup> by using a Biologic VMP 3e potentiostat/galvanostat. The galvanostatic charge/discharge cycling tests were carried out in a split cell with Zn anode, a Whatman separator, and graphene cathode with different electrolytes by using a battery tester Nanocycler from Nanobase.

Phase identification and structural analysis were performed using a Bruker D8 Advance X-ray diffractometer (XRD) fitted with a copper source, CuK $\alpha$  at a wavelength of  $\lambda = 1.5406$  and a LynxEye<sup>TM</sup> silicon strip detector. The patterns were recorded between  $2\theta = 20^{\circ}-80^{\circ}$  in Bragg-Brentano mode with a step size of 0.01°.

XPS Analysis was performed using a Kratos Axis SUPRA XPS fitted with a monochromated Al k $\alpha$  X-ray source (1486.7 eV), a spherical sector analyser and 3 multichannel resistive plate, 128 channel delay line detectors. All data was recorded at 150W and a spot size of 700 x 300  $\mu$ m. Survey scans were recorded at a pass energy of 160 eV, and high-resolution scans recorded at a pass energy of 20 eV. Electronic charge neutralization was achieved using a magnetic immersion lens. Filament current = 0.27 A, charge balance = 3.3 V, filament bias = 3.8 V. All sample data was recorded at a pressure below 10<sup>-8</sup> Torr and a room temperature of 294 K. Data was analysed using CasaXPS v2.3.20PR1.0 and the spectra were calibrated with C1s peak at 284.8 eV.

Raman spectra of graphene were acquired using Renishaw inVia confocal Raman microscope, equipped with a 514 nm laser (Stellar-REN) and using a diffraction grating of 1800 lines/mm with a Renishaw CCD camera as the detector, respectively. For Raman, the samples were run with laser power at 100 % using the 5x objective lens with a 532 nm laser, respectively.

*In-situ* EC-AFM studies were performed using Bruker multimode 8 in contact mode. SNL 10 cantilever with 0.1 N/m force constant was used for imaging. Freshly cleaved HOPG substrate was used as working electrode. 0.5 mm Zinc wire used as counter and reference electrodes. To clean and remove native Zinc Oxide form Zinc wire, it was polished with sandpaper followed by rinsing with isopropanol and Milli-Q water.

## 3. Computational details

Vienna Ab initio Simulation Package (VASP) was used to perform spin polarized periodic density functional theory based quantum chemical calculations [24]. We employed the projector augmented wave (PAW) method, and for the expansion of the plane-wave basis set, the cut-off energy was set to 525 eV, which gave bulk energies converged to within  $10^{-5}$  eV [25]. We chose a convergence criterion of 0.01 eV Å<sup>-1</sup> for the structural optimizations and a gamma centred k-point grid of 5  $\times$  $5 \times 1$  was employed. The revised Perdew-Burke-Ernzerhof (PBE) version of generalized gradient approximation (GGA) for solids i.e., the PBEsol exchange and correlation functional was used to relax the structures and to perform the total energy calculations [26]. In this study, we also used the Grimme's dispersion correction (DFT-D3), as dispersive effects might be significant for the systems under investigation [27]. The 10  $\times$ 10 pristine graphene model was obtained from the bulk graphite structure with a calculated energy minimized lattice constants of  $\mathbf{a} = \mathbf{b}$ = 2.460 Å and c = 6.800 Å (Exp. A = b = 2.461 Å and c = 6.709 Å) [28, 29]. For all our calculations, in the direction perpendicular to the surface we used a vacuum gap of  $\sim 15$  Å, which is sufficient to eliminate any spurious interactions along the z-axis.

## 4. Results and discussion

We first evaluated the bio-ionic liquid electrolyte in a graphene/ graphene symmetric cell to assess its suitability for supercapacitor applications. Fig. 1a shows the cyclic voltammogram (CV) of a 1M Zn acetate + 1.5M choline acetate electrolyte in a symmetric graphene/ graphene electrode setup. 1.5M choline acetate in the aqueous solution was found to be the optimum condition (see Fig. S1) showing high capacitance. The CV in Fig. 1a exhibits typical capacitive behaviour, with clear changes in current response as the scan rate is varied. When performing charge-discharge cycles at various current densities (Fig. 1b and c), a moderate capacitance of 62 F g<sup>-1</sup> is observed at a current density of 0.5 A g<sup>-1</sup> (Fig. 1c), which decreases as the current density increases. The capacitance with the bio-ionic liquid electrolyte is approximately 1.5 times higher than that observed with the 1M Zn acetate aqueous electrolyte at the same current densities (Fig. S2).

Upon adding Choline iodide (ChI) to the electrolyte, a change in the capacitive curves is observed (Fig. 1d). Notably, no redox peaks associated with iodine oxidation/reduction are detected within the tested electrochemical window, suggesting that the iodine redox process does not occur under these conditions. In contrast, experiments with ChI alone in the electrolyte (Fig. S3) show iodine redox peaks near 0 V for lower concentrations of ChI, which likely shifts to more negative potentials upon the addition of Choline acetate (ChAc). Nevertheless, in the presence of both ChAc and ChI, a 20 % enhancement in capacitance is observed across a range of current densities up to 2 A  $g^{-1}$  (Fig. 1e and f).

Next, the electrolytes were tested in Zn-ion capacitors (ZICs) with a Zn anode and graphene cathode to evaluate their suitability for ZIC



**Fig. 1.** (a) CV of graphene-graphene symmetric cell at different scan rates in 1M ZnAc+1.5M ChAc electrolytes (b) Charge discharge of the symmetric cell at different current densities (c) Specific capacity calculated from Fig. 1b at different current densities. (d) CV of graphene-graphene symmetric cell at different scan rates in 1M ZnAc+1.5M ChAc electrolytes+30 mM ChI (e) Charge discharge of the symmetric cell at different current densities (f) Specific capacity calculated from Fig. 1e at different current densities.

applications. To assess the performance of the electrolyte in these systems, we investigated the Zn deposition/stripping behaviour in a Zn/Zn symmetric cell. As shown in Fig. 2a, when cycling in the 1M Zn acetate +1.5M choline acetate electrolyte at a current density of 2 mA cm<sup>-2</sup> and a capacity of 1 mAh cm<sup>-2</sup>, the stability of the Zn deposition/stripping process begins to deteriorate after approximately 70 h. In contrast, when Choline iodide (ChI) is added to the electrolyte, relatively stable Zn deposition/stripping is observed for up to 80 h (Fig. 2b).

Interestingly, while the stability of Zn deposition/stripping diminishes in the 1M ZnAc +1.5M ChAc electrolyte, scanning electron microscopy (SEM) images in Fig. 2c do not show any dendrite formation. Instead, hexagonal faceted platelets are observed, indicating a smooth and stable Zn deposition morphology. A similar morphology is observed when ChI is added to the electrolyte (Fig. 2d), further suggesting that the addition of ChI does not promote dendrite growth. X-ray diffraction (XRD) analysis in Fig. 2e confirms the formation of hexagonal Zn, which is consistent with the standard ICDD Zn data (ICDD 78–9362).

High-resolution X-ray photoelectron spectroscopy (XPS) spectra of the cycled Zn (Fig. 2f) reveal no secondary reactions or formation of undesirable Zn compounds on the surface, indicating that the deposition process remains stable and free from side reactions. The XPS survey spectra in Fig. S4 show the presence of C and O 2p peaks, which are attributed to residual bio-ionic liquid on the surface of the Zn anode.



Zn-graphene electrodes were subsequently tested with bio-ionic

Fig. 2. (a, b) Electrochemical stability of Zn/Zn symmetric cell with 1M ZnAc+1.5M ChAc and 1M ZnAc+1.5M ChAc+30 mM ChI cycled at 2 mA cm<sup>-2</sup> (c and d) SEM of Zn after cycling for 80 h from two different electrolytes (e) XRD of Zn after cycling in two different electrolytes (e) High resolution XPS of Zn 2*p* spectra.

liquid electrolytes, both with and without Choline iodide (ChI). Fig. 3 presents the cyclic voltammetry (CV) and charge-discharge profiles at different scan rates and current densities, respectively. In comparison to the purely capacitive process observed in the symmetric cell, a broad reduction and oxidation process is evident around 0.8 V and 1.2 V along with an oxidation/reduction peak at 1.7 V and 1.39 V at lower scan rates, respectively (Fig. 3a, Fig. S5). This suggests that there is an interaction between Zn complex with bio-ionic liquid and the graphene surface, leading to charge redistribution within the system.

Galvanostatic cycling at various current densities reveals a significant enhancement in storage capacity (Fig. 3b and c). At lower current densities (0.5–3 A  $g^{-1}$ ), a three-fold increase in charge storage capacity is observed (Fig. 3c) compared to the graphene symmetric cell (Fig. 1c). However, at higher current densities  $(>3 \text{ A g}^{-1})$ , the capacity increase is reduced to approximately two-fold. Upon the addition of optimised concentration of ChI to the electrolyte (see Fig. S6 for optimised condition), a clear oxidation/reduction process associated with the  $I^-/I_2^$ redox couple is observed at 1.5 V and 1.0 V, respectively (Fig. 3d). The galvanostatic cycling at different current densities (Fig. 3e) clearly demonstrates a combined battery-supercapacitor type charge-discharge process, which has been previously reported for ionic liquid-based redox-active electrolytes [12,14]. Additionally, an improvement in charge storage is observed in Fig. 3f, where a maximum capacity of 350 F g<sup>-1</sup> is achieved at 0.5 A g<sup>-1</sup>, which decreases to 130 F g<sup>-1</sup> at 5 A g<sup>-1</sup>. The Ragone plot in Fig. S7 shows the energy versus current density wherein an energy density of 80 Wh  $kg^{-1}$  can be achieved at a power density of 2000 W kg<sup>-1</sup>.

To investigate the mechanisms by which the bio-ionic liquid enhances Zn storage in graphene, a series of characterization techniques were employed, including Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and in situ atomic force microscopy (AFM) in conjunction with the density functional theory (DFT) calculations.

Fig. 4 compares the G-band features of graphene in Raman spectra recorded in aqueous, bio-ionic liquid, and redox-active bio-ionic liquid electrolytes. As shown in Fig. 4a, in the aqueous electrolyte, no significant shift in the G band is observed at different charge/discharge potentials. However, peak broadening during discharge and narrowing during the charge process are evident at various potentials. This

behaviour can be attributed to the reduction of graphene oxide present on the cathode during discharge, as previously reported [30-32]. This is further supported by X-ray photoelectron spectroscopy (XPS) data, where a reduction in the C-O and C=O peaks at 286.7 eV and 288.5 eV, respectively, is observed during the discharge process, with peak intensities increasing again during charging (Fig. S8a).

In the presence of Choline acetate (ChAc) in the electrolyte, Fig. 4b shows that the G band exhibits both peak broadening and shifts. The broadening of the peak can be associated with the reduction of C-O and C=O groups in graphene, as confirmed by XPS measurements (Fig. S8b). The shift of the G band towards higher wavenumbers is likely due to charge transfer interactions between graphene and the choline species in the electrolyte.

The presence of ChI in the electrolyte further changes the charge storage mechanism as seen from the Raman spectra in Fig. 4c. During initial discharge (d-1V), an increase in wavenumber is observed which is due to the interaction between solvated Zn and graphene (also confirmed from XPS in Fig. S8c) after which a downshift in the wavenumber is observed during discharge. The decrease can be attributed to the strain within graphene possibly due to the iodine reduction at the surface of graphene [31,33]. Although doping of graphene has shown a shift to lower wavenumbers [33–35], XPS data confirmed that no iodine doping in the graphene occurred as seen from the survey spectra in Fig. S9. On charging, again an increase in the wavenumber in the Raman spectra is observed in Fig. 4c which can be attributed to the release of strain along with the oxidation of iodine.

To understand the interaction between graphene and the electrolyte, DFT based quantum chemical calculations were performed. Since the ChAc, ZnAc and ChI are relatively large molecules, we consider a 10 × 10 supercell of graphene, which allows the accommodation of more than one molecule at a time. The surface coverage, ( $\theta$ ), of these systems are in the range of 0.001–0.015 ML, which is calculated using

$$\theta = n_{N_{\text{atom}}}$$
[1]

where, n and  $N_{\rm atom}$  are the number of adsorbed molecules and number of carbon atoms on the graphene sheet (i.e., 200) respectively. The fully relaxed structures of ZnAc.G (M1), (ZnAc + ChAc).G (M2) and (ZnAc +



**Fig. 3.** (a) CV of Zn-graphene symmetric cell at different scan rates in 1M ZnAc+1.5M ChAc electrolytes (b) Charge discharge of the symmetric cell at different current densities (c) Specific capacity calculated from Fig. 3b at different current densities. (d) CV of graphene-graphene symmetric cell at different scan rates in 1M ZnAc+1.5M ChAc electrolytes+30 mM ChI (e) Charge discharge of the symmetric cell at different current densities (f) Specific capacity calculated from Fig. 3e at different current densities.



Fig. 4. Raman spectra shift in G band of graphene at different charge discharge potentials (d-represents discharge process and c-represents charge process) in (a) 1M ZnAc (b) 1M ZnAc+1.5M ChAc and (c) 1M ZnAc+1.5M ChAc+30 mM ChI.

ChAc + ChI).G (M3) systems are shown in Fig. S10.

To access the stability of the systems the adsorption energy  $(E_{ad})$ , is calculated using equation (2) wherein the interaction energy  $(E_{int.})$  arise due to the interaction between the adsorbates and the adsorbent and the lateral interaction energy  $(E_{Lat.})$  due to the interaction between the adsorbates themselves [36].

$$E_{ad} = [E_{Int.} + E_{Lat.}],$$
<sup>[2]</sup>

The  $E_{Int.}$  and  $E_{Lat.}$  are calculated using equations (3) and (4):

$$E_{Int.} = [E(M.G) - E(G//M.G) - E(M//M.G)]/n,$$
[3]

$$E_{Lat} = [E(M//M.G) - E(M)]/n,$$
 [4]

where, E(M.G) is the energy of the total system i.e., molecules on the graphene sheet, E(G//M.G) and E(M//M.G) are the total energy of the graphene surface and the adsorbed molecules at the configuration of the total system and E(M) is the total energy of the fully relaxed adsorbates.

It is seen that the interaction energies of the adsorbates with graphene is in the order of M3 ( $E_{int.} = -0.725 \text{ eV/molecule}$ ) > M2 ( $E_{int.} = -0.642 \text{ eV/molecule}$ ) > M1 ( $E_{int.} = -0.469 \text{ eV/molecule}$ ). Additionally, while the shortest distance between the ZnAc and the graphene surface in M1 is 2.920 Å, in the M2 and M3 it is in the range of 2.295–2.320 Å. This shows that the ZnAc molecule is relatively weakly adsorbed on graphene and therefore, leads to a lower capacity as seen in Fig. S2 and does not result in any Raman shift (Fig. 4a). In comparison, the interaction energies appear to be more negative in the presence of the ChAc and ChI molecules, resulting in the shift of the Raman peaks in Fig. 4b and c and improvement in capacity as seen in Fig. 3. We further investigate the change in the electronic structure of the graphene surface by visualising the isosurfaces of the charge density difference ( $\rho_{diff}$ ) in these systems using equation (5):

$$\rho_{\rm diff} = \rho_{\rm M,G} - \rho_{\rm G} - \rho_{\rm M},\tag{5}$$

Here,  $\rho_{M,G}$ ,  $\rho_G$ , and  $\rho_M$  are the charge density of the total system, graphene and the adsorbed molecule(s) respectively [37–40].

From the  $\rho_{diff}$  plots in Fig. 5(a–c), we find that in M2 and M3 there is a significant charge redistribution i.e., charge accumulation (in blue) and depletion (in green) on the graphene surface, which may result in weakening of some of the graphene C = C bonds. To clearly visualise the effect of charge redistribution on the graphene C = C bonds we calculate the electron localisation function (ELF) using equations (6)–(8):

$$\mathrm{ELF} = \frac{1}{1 + \left(\frac{D}{D_h}\right)^2},$$
[6]

$$D = \frac{1}{2} \sum_{i} |\nabla \phi_{i}|^{2} - \frac{1}{8} \frac{|\nabla \rho(\mathbf{r})|^{2}}{\rho(\mathbf{r})}$$
[7]

$$D_{h} = \frac{3}{10} \left(3\pi^{2}\right)^{5/3} \rho(\mathbf{r})^{5/3},$$
[8]

where,  $\phi_i$  and  $\rho(\mathbf{r})$  are the Kohn Sham orbitals and electron density respectively [30]. The ELF values are between 0 (no bond) and 1 (strong bond). As shown in Fig. 5(d–f), we see strong C = C bonds in M1 but in M2 and M3 there are regions of weakened C = C bonds due to the presence of the adsorbates. The atom projected density of states (pDOS) of the two nearest C atoms in the graphene surface from the adsorbates is shown in Fig. 6a-c wherein for M1 the *p*-orbital signatures of these are completely superimposed (Fig. 6a) whereas for M2 and M3 the *p*-orbital signatures of one of the C-atoms is slightly lower than the other (Fig. 6b and c). To quantify this observation, we calculate the area under the *p*-orbital signatures (A) of the C-atoms using equation (9):

$$A = \frac{1}{2} \int_{-\infty}^{\infty} (P_1 + P_2) . dE,$$
 [9]

here,  $P_1$  and  $P_2$  respectively are the number of states of the first and the second carbon atoms under consideration. Our calculation reveals that  $A_{M1}$  (1.026 number of states/C-atom) >  $A_{M2}$  (0.992 number of states/C-atom) ~  $A_{M3}$  (0.942 number of states/C-atom), meaning that the C = C bonds in graphene bonds are weakened in M2 and M3 agreeing well



Fig. 5. Isosurface ( $\sim 10^{-3}$  e/Å<sup>3</sup>) of  $\rho_{diff}$  in M1, (a) M2 and (b) M3. ELF of (d) M1, (e) M2 and (f) M3.



Fig. 6. pDOS of two nearest C-atoms from the adsorbates in (a) M1, (b) M2 and (c) M3. Spin density isosurfaces  $(10^{-5} \text{ e/Å}^3)$  of the adsorbates in (d) M2 and (e) M3.

with our analyses on  $\rho_{diff}$  and ELF. Thus, based on these theoretical calculations and Raman spectra, it is evident that the presence of Choline affects the local electronic structure of graphene, which enhances the charge storage characteristics of graphene.

Finally, to investigate the influence of Choline iodide (ChI) on the Raman spectra and capacitance, we calculated the lateral interaction energies in models M2 and M3 using equation (4). In M2, which includes Zn acetate (ZnAc) and Choline acetate (ChAc), we find that the molecules interact more strongly, with a lateral interaction energy of  $E_{Lat} = -0.203 \text{ eV/molecule}$ . In contrast, in M3, where ZnAc, ChAc, and ChI are

present, the interaction energy decreases to  $E_{Lat} = -0.108 \text{ eV/molecule}$ . This reduction in lateral interaction energy in M3 can be attributed to the presence of the electronegative iodide ion (I<sup>-</sup>) in ChI, which weakens the interaction between ChAc and ZnAc molecules. This is further confirmed by the spin density plots in Fig. 6d and e, which show that in M2, the spin densities of ChAc and ZnAc are delocalized over both molecules. In M3, however, the spin density is predominantly localized on the ChI molecule, indicating a weakened lateral interaction between ZnAc and ChI.

The decrease in lateral interaction in M3 likely facilitates the iodine

redox process on the graphene surface, contributing to the observed increase in storage capacity and the shifts in the Raman spectra at certain electrode potentials, as shown in Fig. 4c.

To further investigate the electrode-electrolyte interactions and the morphological changes of graphene in the presence of the bio-ionic liquid containing redox-active species, in-situ electrochemical atomic force microscopy (AFM) experiments were conducted on highly oriented pyrolytic graphite (HOPG). Fig. 7 presents the cyclic voltammogram (CV) obtained in the AFM electrochemical cell, along with in-situ AFM images captured at different potentials. In the double-layer region (0.87 V and 1.27 V, shown in Fig. 7a and b), the HOPG substrate clearly exhibits layering of 1–2 nm (Fig. S11a) in height which indicates the presence of Zn-complexed molecules in presence of choline [41].

As the substrate potential is increased to the peak oxidation potential (1.87 V, Fig. 7c), significant changes in the surface morphology of the HOPG terrace are observed, with the formation of layers having 2–5 nm thickness (Fig. S11b). These changes can be attributed to the adsorption of the bio-ionic liquid along with Zn complexes, which alters the local electron density of HOPG, consistent with both the Raman and DFT studies. The surface adsorption further intensifies when the potential is increased to 2.12 V (Fig. S11c).

To investigate the effect of electrolyte decomposition on HOPG, the electrode potential was further raised to 2.37 V, at which point the HOPG step-edge structure disappears irreversibly (Fig. 7e). During the discharge process, a periodic wavy structure is observed around 1.87 V in the cathodic scan and at lower potentials (Fig. 7g and h). These in-situ electrochemical AFM results confirm that the redox-active bio-ionic liquid adsorbs onto the HOPG surface, causing significant morphological changes during the electrochemical process. The findings also suggest that the operational voltage of the Zn-graphene capacitor should be limited to 2.1 V, beyond which irreversible surface modifications are likely to occur. Experiments conducted at lower reversible potential of 2.24 V (see Fig. S12) showed much higher reversibility of HOPG surface.

However, some irreversibility on HOPG occurs during cycling which might be due to adsorption of complexes on the surface.

Finally, the fabricated Zn-graphene capacitor was tested for stability over a voltage range of 0–1.9 V. Fig. 8 presents the cyclability of the capacitor in different electrolytes at various current densities, both with and without Choline iodide (ChI) in the electrolyte. Fig. 8a and b compare the capacitance at a current density of 3 A g<sup>-1</sup> for the 1M Zn acetate +1.5M Choline acetate electrolyte and the 1M Zn acetate +1.5M Choline acetate +30 mM ChI electrolyte, respectively.

It is evident that, without Choline iodide (ChI), the capacity reaches 70 F  $g^{-1}$ , which decreases to approximately 55 F  $g^{-1}$  after 3000 cycles. In the presence of ChI in the electrolyte, a higher initial capacity of 160 F  $g^{-1}$  is observed, which decreases to 130 F  $g^{-1}$  after 5000 cycles. At a lower current density of 1 A  $g^{-1}$ , the redox-active electrolyte initially delivers a capacity exceeding 200 F  $g^{-1}$ , which drops to 175 F  $g^{-1}$  after 400 cycles. When the same experiments are performed at 0.5 A g<sup>-1</sup>, the initial capacity reaches 350 F g<sup>-1</sup>, which decreases to 270 F g<sup>-1</sup> after 400 cycles. These stability results suggest that the capacity obtained with the redox-active bio-ionic liquids is comparable to that of other electrolytes (see Table S1 for comparison), highlighting the potential of this approach in developing environmentally benign Zn-ion capacitors (ZICs). The decrease in the capacity with cycling might be related to some surface changes taking place on the graphene as seen from in situ AFM studies. Additionally, there might be some decomposition of electrolyte with cycling which affects the capacity which will need further investigation. It is expected that by tuning the graphene or by using modified carbon cathodes [42-44], further improvement in the capacity can be achieved.

#### 5. Conclusions

In conclusion, we have demonstrated the use of a redox-active bioionic liquid electrolyte for Zinc-ion capacitors (ZICs). Compared to



Fig. 7. In-situ Electrochemical AFM study of Zn/HOPG with 1M ZnAc +0.15 M ChAc +0.015 M ChI electrolyte, Cyclic voltammogram, (a–h) In-situ Electrochemical AFM images with different potentials applied on the sample.



**Fig. 8.** Cycling of Zn-graphene in (a) 1M ZnAc+1.5M ChAc electrolyte at a current density of 3A  $g^{-1}$  (b) 1M ZnAc+1.5M ChAc+30 mM ChI electrolyte at a current density of 3A  $g^{-1}$  (c) 1M ZnAc+1.5M ChAc+30 mM ChI electrolyte at a current density of 1A  $g^{-1}$  (d) 1M ZnAc+1.5M ChAc+30 mM ChI electrolyte at a current density of 0.5A  $g^{-1}$ .

aqueous electrolytes, the bio-ionic liquid exhibits a stronger interaction with graphene, facilitating charge transfer processes that enhance the capacitance of the ZICs. The incorporation of Choline iodide (ChI) into the electrolyte induces oxidation/reduction reactions on the graphene surface, further improving capacitance. The specific capacitance values achieved are comparable to those obtained with traditional acidic electrolytes. This work highlights an effective strategy for developing environmentally benign, redox-active electrolytes and paves the way for the creation of more sustainable energy storage systems.

#### CRediT authorship contribution statement

Sumana Brahma: Investigation, Validation, Methodology, Formal analysis, Data curation, Writing – review & editing. Arpita Panda: Methodology, Investigation, Data curation, Writing – review & editing Veerabhadrarao Kaliginedi: Writing – review & editing, Methodology, Investigation. Arunabhiram Chutia: Conceptualization, Writing – review & editing, Methodology, Investigation. Abhishek Lahiri: Conceptualization, Supervision, Writing – review & editing, Methodology, Investigation.

## Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Abhishek Lahiri reports financial support was provided by Engineering and Physical Sciences Research Council. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jpowsour.2025.236843.

#### Data availability

The link to the data is provided in 10.17633/rd.brunel.27901281

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