A new generation high-performance supercapacitor engaging redox property of solvent-electrolyte (Ionic Liquid)

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Abstract: A proof of concept to enhance the specific capacitance and energy density of a supercapacitor has been demonstrated wherein reversible 1e⁻ transfer redox chemistry of cations of ionic liquids ([EMIM][EtSO₄] and [MIM][HSO₄]) which acted as both solvent and electrolyte has been utilized. Outstanding specific capacitance and energy densities in the range of 420-710 F/g and 580-920 Wh/kg, respectively, have been obtained for carbon-based nanomaterials.

Introduction: The rapid industrial development in the last few decades resulted in global warming due to excessive emission of CO₂ and has now become a threat to human civilization.¹⁻⁴ In consequence, the world is promptly trying to move towards renewable energy resources. In this regard, supercapacitors are playing a leading role which act as short-term power sources in electronic devices such as hybrid electric vehicles, portable electronics, aeronautics etc.⁵⁻⁶ Traditionally, supercapacitors utilize electrical double-layer formation at the electrode/electrolyte interface due to electrolyte ion accumulation under the application of an electric field.⁷ The enhancement of charge storage capacity is usually achieved by synthesizing high surface area microporous materials, which improves ion accumulation capacity manifold.⁸ However, scientists

quickly realized two key challenges of this field, and they are: (a) only double-layer formation cannot lead to very high charge storage capacity due to the limitation of ion accumulation on materials' surfaces, and (b) energy density of supercapacitors remained low due to the narrow potential stability window of aqueous electrolytes.⁹⁻¹² In order to resolve the first challenge, pseudocapacitors were introduced wherein electron transfer at the electrode/electrolyte interface provided additional charge storage capacity.^{5, 13} Different metal oxides were utilized for this purpose, among which RuO_2 provided very high specific capacitance due to several redox transitions.¹⁴⁻¹⁵ In 2011, Santamaria and co-workers introduced a new innovative strategy to improve charge storage capacity further, wherein redox active additive (hydroquinone) was added in the electrolyte solution, which provided very high specific capacitance (~900 F/g) for different carbon-based materials due to electron transfer (2H⁺/2e⁻ proton-coupled electron transfer (PCET)) property of redox additive which otherwise had significantly low specific capacitances (< 300 F/g).¹¹

In order to enhance the energy density of a supercapacitor, ionic liquids (ILs) are often used as both solvent and electrolyte in supercapacitors since ILs have significantly high electrochemical potential stability.¹⁶ ILs are also attractive due to their non-volatility, nonflammability, and asymmetric cation/anion interaction etc.¹⁷⁻²¹ However, ILs have low electrical conductivity and high viscosity, which increases ion-transport resistance, but these shortcomings can be minimized using ILs based on imidazolium cations.¹⁷⁻²¹ Moreover, other attractive properties of ILs, such as electrochemical stability, thermal resistance properties etc., can overshadow its limitations.^{17, 22}

In the field of supercapacitors, to date, it is a natural concept to maximize the oxidation/reduction resistance of electrolytes and solvents since irreversible oxidation/reduction of solvent or electrolyte can hamper the cyclic stability and will result in rapid degradation of supercapacitors.¹⁶

In this work, we present an innovative proof of concept to demonstrate high-performance supercapacitors based on carbon-based materials with ILs as both solvent and electrolyte, wherein ILs undergo reversible redox transitions that improve both specific capacitances and energy densities remarkably. For supercapacitor electrodes preparation, previously reported oxygen-functionalized graphene (OFG),²³ and immense microporous carbon (IMC)²⁴ from our group were chosen as electrode materials, while ILs were 1-ethyl 3-methyl imidazolium ethyl sulphate ([EMIM][EtSO4]) and 1-methyl imidazolium sulfate ([MIM][HSO4]. These ILs undergo a reversible 1e⁻ electro-reduction to generate a radical cation species which can be stable in electrochemical conditions.²⁵ Consequently, remarkably high specific capacitances in the range of 5305-474 F/g have been achieved, while exceptional energy densities in the range of 5308-871 Wh/kg were non-halogenated and hence can eliminate the ease of anodic oxidation at low potentials.²² Moreover, nonhalogenated ILs are also environmentally friendly. In the next few sections, we discuss the synthesis, electrochemical results, and important conclusions to establish this new concept in the field of supercapacitors.



Scheme 1: Molecular structure of material used in this work: (a) OFG. Molecular structure of ILs:(b) [EMIM][EtSO₄], and (c) [MIM][HSO₄].

Results and Discussions: Oxygen-functionalized graphene (OFG) was synthesized following a literature procedure previously reported by our group, and it has hydroxyl, carbonyl, and carboxylic acid functionalization on the sheet edges as shown in Scheme 1a.^{23, 26} OFG consists of 3-4 layers of such sheets having an interlayer distance of 3.6 Å.²³ It was deposited on Pt electrode surface employing a drop-casting method with polyvinylidene fluoride (PVDF) as a binder with a typical mass loading of 0.7 mg/cm² on each electrode. Two such electrodes were pressed on the Swagelok cell with a Whatmann paper separator for supercapacitor testing. These Whatmann papers were soaked with different solvents/electrolytes and used for supercapacitor experiments in a two-electrodes set-up. All the synthesis details, supercapacitor electrode preparation, and calculation methodologies are provided in the Supporting Information (SI). For electrochemical studies, apart from ILs, 1 M H_2SO_4 in aqueous electrolyte and acetonitrile having 0.5 M tetrabutylammonium hexafluorophosphate (TBAPF₆) were also used for comparison. Supercapacitor performance of OFG revealed only 147 F/g specific capacitance at 10 mV/s in an aqueous electrolyte having 2 M H₂SO₄ electrolyte with a potential window of 1 V (Figure 1a). CV results translate to the highest energy and power densities of 10.6 Wh/kg and 3.1 kW/kg, respectively (Figure S1, Table S1, SI). The weak peak observed at 0.3 V was due to the redox chemistry of oxygen functionalization of OFG.²³ Upon changing the solvent to nonaqueous acetonitrile solvent with 0.5 M TBAPF₆, the specific capacitance was further reduced to 92 F/g (Figure 1b). However, the highest energy and power densities were improved up to 58.8 Wh/kg and 4.5 kW/kg, since the potential window was enhanced to 2.8 V in nonaqueous solvent (Figure S2, Table S2, SI).



Figure 1: Cyclic voltammogram at 10 mVs⁻¹ scan rate with OFG in (a) 2 M H₂SO₄, (b) acetonitrile with 0.5 M TBAPF₆, and (c) neat [EMIM][EtSO₄] electrolytes.



Scheme 2: Proposed mechanism for radical cation formation during reduction of EMIM⁺.

Next, the experiments were performed using neat [EMIM][EtSO₄] IL, and the specific capacitance improved remarkably with a value of 325 F/g at 10 mV/s scan rate and 400 F/g at 5 mV/s scan rate (Figures 1c, S3, Table S3, SI). Even more importantly, the potential window was enhanced to 5.6 V. Hence, the maximum energy and power densities reached extraordinary values of 871 Wh/kg and 20.6 kW/kg, respectively (Table S3, SI). Nearly three-fold specific capacitance and ten-fold energy density enhancements were presumably due to the reversible one-electron transfer redox chemistry of IL cation, i.e., EMIM⁺, as evidenced by the strong peak observed in Figure 1c. EMIM⁺ can undergo 1e⁻ reduction to generate a radical cation (EMIM⁺), and the unpaired electron

is delocalized among three atoms of the imidazolium ring, which can provide stability to the radical cation in the electrochemical time-scale (Scheme 2a). Recent research on the stability of imidazolium radical cations have been discussed by Mandal et. al.²⁷, Han et. al.²⁸ etc. However, the stability of the radical cation herein could be due to two additional reasons and they are (a) electrochemistry was performed in an air-tight cell, and (b) even more importantly, the formation of these radicals occurred inside the confined nanopores of the OFG which presumably provided stability to the radical cation and avoided further reaction. The separation of peaks was large because of the high viscosity and poor conductivity of IL. This type of reversible redox chemistry provided a massive improvement in the specific capacitance value since IL is present in a comparatively large quantity in the system. At this juncture, it is of paramount interest to establish the stability of ILs new formation during long-term electrochemical experiments, and the proofs for the stability of ILs have been provided in the next few sections (vide infra).



Figure 2: Supercapacitor performance of OFG in [EMIM][EtSO₄] IL: (a) GCD overlay at 5 and 2 Ag⁻¹, (b) capacitive retention at different scan rates of CV, (c) Nyquist plot (inset high frequency region), and (d) cyclic test at 100 mVs⁻¹ scan rate for 3000 cycles (inset overlay of CVs at different cycles).

In order to further confirm the supercapacitor performance of OFG in [EMIM][EtSO₄], experiments were also conducted employing galvanostatic charge/discharge (GCD) experiments (Figures 2a and S3, SI). GCD results revealed plateaus during the charging, and discharging process, which is a signature of electron transfer due to EMIM⁺ (Figures 2a, S3, SI) and specific capacitance values were similar to CVs (Table S3, SI). The retention of specific capacitance with increasing current density of GCDs was 31% (Figure 2b), and this low value was presumably due to the inferior ionic conductivity of IL. Figure 2c shows the Nyquist plot of electrochemical impedance spectroscopy (EIS) studies conducted at 0 V, and the rise of impedance in the lowfrequency region was reasonably sharp along the imaginary axis, suggesting decent diffusional behavior. The inset of Figure 2c shows the zoomed-in high-frequency region of the Nyquist plot, and the arrow shows a knee frequency of 38.5 Hz, which is defined as the frequency at which diffusion of electrolyte starts inside the nanomaterials.²⁹⁻³⁰ EIS results were fitted with an equivalent circuit diagram (Figure S4, SI), and all the fitted parameters are summarized in Table S4, SI. Briefly, the solution resistance (R_s) was high due to the low conductivity of IL, however the charge transfer resistance at the electrode/electrolyte interface (R_{ct}) was relatively low (17.2 Ω), implying ease of electron transfer at the interface for this IL (Table S4, SI). The long-term performance of this supercapacitor was tested by performing a cyclic test at 100 mV/s for 2500 cycles (Figure 2d), and remarkable capacitance retention of 82.6% was observed. The inset of Figure 2d shows the CVs obtained at 1st, 1500th, and 2500th cycles, and the peak positions remained unaltered, which provides the first evidence that the IL did not decompose/degrade even after a long time of the experiment. However, the peak intensity declined during the cyclic test, but the decline was not significant. It is important to emphasize that this experiment took more than three days to complete.



Fig 3: NMR spectra of [EMIM][EtSO₄] before and after cyclic test.

Next, to provide further evidence of IL stability during electrochemistry, NMR studies were performed. Figure 3 shows the ¹H NMR spectrum of as-synthesized [EMIM][EtSO₄]. After the cyclic test, the Whatmann filter paper was washed with deuterated chloroform (CDCl₃), and ¹H NMR was taken, which revealed the presence of all the peaks for IL with the same intensity ratio (Figure 3). One extra peak at 2.39 ppm was due to the adsorbed water during the recovery of IL. Furthermore, this IL's FT-IR spectra were taken before and after the cyclic test, and all the peaks remained intact, which further confirmed the stability of IL (Figure S5, SI).

Next, to further bolster these exciting observations, supercapacitor performance was tested with OFG as nanomaterial in [MIM][HSO4] IL (Scheme 1c). Electrochemical results revealed a similar high specific capacitance of 474 F/g at 5 mV/s with strong redox peaks due to cation of IL, i.e., MIM⁺, which can undergo 1e⁻ reduction redox chemistry similar to MIM⁺ (Figure S6, Table S5, SI). With [MIM] [HSO4], the highest energy density was 581 Wh/kg (Table S5, SI), and the potential window was 4.2 V (Figure S6, SI). The cyclic performance of the material was tested for 2500 cycles at a scan rate of 100 mV/s, and it revealed excellent capacitance retention of 75.4%

(Figure S6d, SI). CV features remained unaltered during the cyclic test, which provides evidence for the stability of IL during the cyclic test (Figure S6d, SI). Furthermore, NMR and IR results before and after the cyclic test again suggested that the [MIM] [HSO4] didn't decompose during the cyclic test as well (Figure S7, SI). To further bolster this chemistry, experiments were conducted with another carbon-based material, i.e., immense microporous carbon (IMC) in [EMIM][EtSO4]. A high specific capacitance (305 F/g) with a similar electrochemical feature was observed for IMC in [EMIM][EtSO4] (Figure S9, Table S6, SI). The highest energy and power densities for IMC in [MIM][HSO4] were 530 Wh/kg and 23.6 kW/kg, respectively (Table S6, SI).



Figure 4: Ragone plot for supercapacitor device having ILs as electrolytic system with OFG electrode material and compared with literature having different ionic liquids with carbon-based electrode materials.

Finally, Ragone plots for OFG in two different ILs ([EMIM][EtSO₄] and [MIM][HSO₄]) are shown in Figure 4 and compared with literature reports,^{6, 31-35} which show significantly higher energy and power densities for OFG in these ILs compared to previous reports (Table S7, SI).¹⁶ In fact, energy densities obtained in this work are 5-9 times better than previous best reports (Table S7, SI) and were even higher than batteries.¹⁶ The highest energy densities of OFG in

[EMIM][EtSO₄] and [MIM][HSO₄] were 871 and 581 Wh/kg, while the power densities were 20.6 and 18.9 kW/kg, respectively (Tables S3 and S5, SI).

Conclusions: In conclusion, a proof of concept has been presented herein, which involves reversible electron transfer properties of ILs, which acted as both solvent and electrolyte for remarkable enhancement of specific capacitances and energy densities of electrode materials for supercapacitor application. ILs such as [EMIM][EtSO4] and [MIM][HSO4] have been used while the electrode materials were oxygen functionalized graphene (OFG) and immense microporous carbon (IMC). Specific capacitance and energy densities in the range of 305-474 F/g and 530-871 Wh/kg, respectively, have been obtained for OFG/IMC, which otherwise have these values in the range of (100-150) F/g and (10-60) Wh/kg respectively in aqueous and nonaqueous electrolyte systems. The chemistry behind this achievement was that the cations of ILs undergo reversible 1e⁻ reduction which are present in large quantities. Moreover, the very high potential stability window of ILs, helped to achieve outstanding energy densities. These findings are truly remarkable and fundamentally can be extended further. Indeed, the coming days seem bright for supercapacitor applications, and future research will shed light on this forecast.

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