



Efficient Electrode Material based on Carbon Cloth Supported Polyaniline/Reduced Graphene Oxide Composites for Supercapacitor Application

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Nowadays, world energy infrastructure is being stretched due to imbalance between energy production and energy consumption; renewable & sustainable energy storage and conversion techniques could resolve this issue. Thus global energy requirements, limited availability of fossil fuels and environmental crisis drive the expansion of alternative or non-conventional energy sources with high energy and power densities. Electrochemical capacitors or supercapacitors, with a combined form of high power density and energy density, have acquired a stunning acceptance towards the field of electrochemical energy storage. Supercapacitors are used in electric vehicles, mobile phones, digital cameras, wearable devices, portable devices and uninterruptible power supplies (UPS) *etc.* Here, we have reported the binder free carbon cloth supported polyaniline/reduced graphene oxide (PRGO) composite hydrogel as a high performance supercapacitor electrode synthesized by a facile chemical polymerization method using phytic acid (PA). The electrochemical performance of binder free carbon cloth based PRGO composite hydrogel electrode has been analysed using cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) techniques. The high specific capacitance (C_S) ~ 235.32 F/g has been obtained for the PRGO composite hydrogel @cc in 1 M H_2SO_4 . The electrochemical results show that the binder free carbon cloth based PRGO composite hydrogel electrode is a promising candidate for supercapacitors.

Keywords: supercapacitor, conducting polymer hydrogels, polyaniline, reduced graphene oxide

1 Introduction

The global energy requirements, limited availability of fossil fuels and environmental crisis drive the search for alternative or non-conventional energy sources having high energy and power densities. Fuel cells, batteries and supercapacitors have attracted attention being the typical non-conventional energy storage devices based on the principle of electrochemical energy conversion. Electrochemical capacitors or supercapacitors especially have acquired immense recognition as energy storage systems due to their capability of meeting the requirements¹. Electrochemical capacitors/supercapacitors are energy harvesting devices competent to quick charge/discharge and capable of delivering higher power than rechargeable batteries². A supercapacitor is lighter than a battery, can operate at low temperatures and no chemical reaction takes place as in case of batteries. Supercapacitors may find applications in uninterruptible power supplies (UPS), digital cameras, mobile phones, electric/hybrid vehicles *etc.*^{3,4}.

The performance characteristics of energy devices are fundamentally determined by the

structural and electrochemical properties of electrode materials. The capacitance of supercapacitor is due to two mechanisms first is the electrochemical double layer formation at the electrode/electrolyte interface^{5,6} and second is due to reversible redox reactions. The electrode material for supercapacitor may be broadly classified into three major categories, namely metal oxides/hydroxides, conjugated polymers and carbon-based materials. The performance of electrochemical energy storage system can be evaluated in terms of the chemical/physical properties of the electrode materials. Thus, the research of new innovative electrode materials is essential for significant improvement in the functioning of supercapacitor.

The conjugated polymers such as polypyrrole (PPy), polyaniline (PAni) and poly(thiophene) require special attention due to, large capacity for energy storage, higher conductivity, facile synthesis, lower cost⁷ and potential applications⁸⁻¹¹. Conducting polymers are reported to have good electrochemical activity¹² and conducting polymer based composite as promising electrodes for hybrid capacitors¹³. Conducting polymer hydrogels (CPHs) are one of the best selections as an electrode material for high performance

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supercapacitors. Conducting polymer hydrogels unite the optical and electrical properties of organic conductors along with the features of hydrogels, expressed significant importance in many energy storage devices. CPHs are three-dimensional arrangement of highly cross-linked system of polymer chains at both micro-scale and nanometer levels with high level of hydration. Polyaniline hydrogel (PHG) due to superficial processibility, high electrical conductivity, redox behaviour and environmental stability is the mostly studied electro-active material¹⁴. To facilitate the electrochemical properties, consolidation of carbon nano-materials into polyaniline based nanostructures has been proved as a promising approach¹⁵⁻¹⁷. It is reported that the incorporation of graphene into conducting polymers and/or TMOs enhanced the electrochemical performance due to increase in the conductivity¹⁸. Graphene being a 2D mono-atomic thick layer of sp^2 bonded carbon atoms is highly conducting and having high surface area ($\sim 2300 \text{ m}^2/\text{g}$), acts as a very good carbon substrate^{19,20}.

Accordingly, the main focus is to develop binder-free electrode materials for high performance supercapacitors. Present work is devoted to the supercapacitive performance of conducting polyaniline/graphene composite hydrogel at carbon cloth electrode. Polyaniline/reduced graphene oxide (PRGO) composite hydrogel has been synthesized by a facile chemical polymerization method using phytic acid (PA). In this work, the gelation and solvation properties of phytic acid have been utilized in a synergetic way to design the conductive nano-structured hydrogel. It has been examined that the synthesis of polyaniline/reduced graphene oxide composite hydrogel in the presence of carbon cloth upgrades the interaction between polyaniline, RGO and carbon clothes correspondingly exceed electron transfer. The binary PRGO composite hydrogel showed good electrochemical results such as high specific capacitance.

2 Experimental

a. Materials

Phytic acid (PA) 50% (w/w) in H_2O (Sigma-Aldrich), graphite flakes (Himedia), monomer aniline (fisher scientific), ammonium per sulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (APS), sulfuric acid (H_2SO_4), hydrochloric acid (HCl), potassium permanganate (KMnO_4), hydrogen peroxide (H_2O_2) and hydrazine hydrate ($\text{H}_6\text{N}_2\text{O}$)

from Merck India have been used for synthesis. All the chemicals and reagents are of analytical grade and were used as such without further purification.

b. Synthesis of Reduced Graphene Oxide (RGO)

Firstly, graphene oxide (GO) was synthesized by modified Hummer's method^{21,22}. Thereafter, graphene oxide was diluted to a concentration of $1\text{g}/100\text{ml}$ and the homogenous colloidal suspension was obtained by dispersing in an ultrasonicator for 30 minutes. Hydrazine hydrate (10 ml) was added to the mixture and stirring continued for 3 hours at a temperature 90°C . The black colored precipitates of RGO so acquired were washed with distilled water, filtered and dehydrated in an oven at 80°C .

c. Synthesis of Polyaniline/Reduced Graphene Oxide Composite Hydrogel

Polyaniline/reduced graphene oxide (PRGO) composite hydrogel was synthesized by an easy and fast synthetic route. In a typical synthesis, 0.458 mL (5 mmol) aniline, 0.921 mL (1mM) phytic acid and RGO (10 wt. \% aniline) were dissolved in 2 mL DI water in the presence of carbon cloth as shown in Fig. 1(a). The solution was placed in a sonicator for half an hour for good dispersion on carbon cloth and cooled to 4°C . Into this, pre cooled solution of 0.286 g (1.25 mM) ammonium per sulphate was added quickly. This result in sudden polymerization resulting in formation of PRGO composite hydrogel formed within three minutes as confirmed by the tube-inversion method. The hydrogel was purified by immersing in distilled water for 24 hours and dried in oven. The polymer coated carbon cloth was further used for electrochemical characterization whereas leftover powdered composite is used for other characterizations. Further, polyaniline hydrogel (PHG) was also synthesized without RGO by the same method with phytic acid.

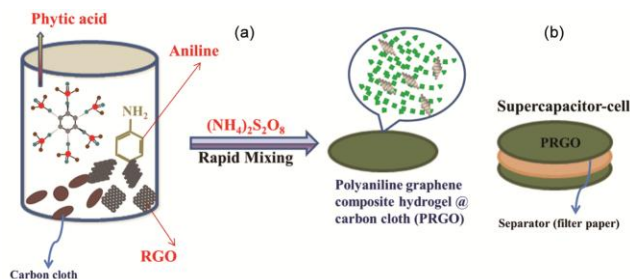


Fig. 1 — Schematic representation of the fabrication of PRGO composite hydrogel electrode (a) and (b) assembling in a cell.

d. Characterization

The formation of GO, RGO, PHG and PRGO composite hydrogel was confirmed by X-ray diffraction (XRD) measurement carried out on Rigaku MiniFlex 600 in scattering range (2θ) of $10\text{--}70^\circ$ using Cu K α -radiation ($\lambda = 1.540598 \text{ \AA}$). The morphology of the as prepared samples was determined scanning electron microscope (SEM). All the above measurements were carried out on composite hydrogel without carbon cloth, whereas electrochemical measurements were realized on composite hydrogel coated carbon cloth (electrode) in specially designed swagelok cell on electrochemical Analyzer (Biologic, Model: VMP 300).

e. Supercapacitor Electrode Assembly

Electrochemical measurements were performed by cutting down two circular discs from PRGO composite hydrogel coated carbon cloth and What man filter paper soaked in 1.0 M H₂SO₄ aqueous electrolyte was used as separator. Subsequently, as shown in Fig. 1(b), the two electrodes were sandwiched into a layered structure. The CV investigations were accomplished between -0.2 and 0.8 V at different scan rates from 20 to 100 mV s^{-1} and GCD was note down in a potential window between 0 and 0.8 V at $0.25\text{--}7.5 \text{ A/g}$ and. All measurements were performed at room temperature. The hydrogel samples coated on carbon cloth were observed to be flexible in nature. Figs. 2(a-d) shows the PRGO@cc electrode bent at various angles and excellent adhesion of polymer composite on carbon cloth was observed as no particles were detached during bending/folding process. Thus, binder free

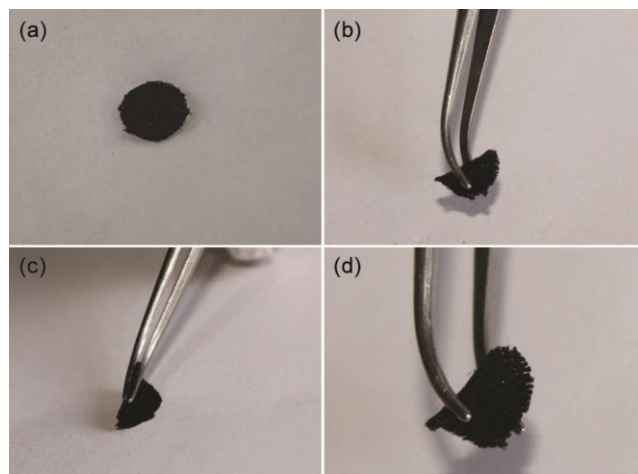


Fig. 2 — (a – d) Photographs of flexible and binder-free PRGO@cc electrode bent at different angles.

PRGO@cc electrode work well as an electrode in flexible supercapacitor.

3 Results and Discussion

In the synthesis of PRGO, phytic acid works as a gelator to form hydrogel as well as a dispersing agent for RGO in aqueous solution of aniline. Simultaneously, it works as a capping agent to prevent RGO from agglomeration during polymerization. In phytic acid, the bound water molecules associated with phosphorous acid groups provide an intensely hydrated interface²³. The phytic acid disperses RGO and dissolves aniline, thereafter APS as oxidising agent is instigated into the mixed solution resulting in quick polymerization to form PRGO nano-structured composite hydrogel. After the polymerization, phytic acid interacts with several polyaniline chains through the lone pair on the nitrogen atom of the aniline unit as well as generating hydrogen bond with neighbouring phytate moiety, thereby, resulting in generation of a mesh-like network. This porous conducting structure of active medium encourages the fast transfer of electron thus improving the electrochemical capabilities. Furthermore, in conjugated polymer based electrodes, the capacitive behaviour is due the redox reactions and takes place near the surface of active medium (pseudocapacitance phenomenon). Consequently, larger area of active material participate in redox reaction because of availability of smaller diffusion route is for electrolyte ions to interact with the electro-active surface of PRGO. As compared to PHG, PRGO hydrogel exhibits more conducting networks because of the presence of RGO. The order of conductivity of PHG and PRGO composite hydrogel were 0.08 and 0.28 S/cm respectively.

a. XRD Studies

To have an insight into the structure of hydrogels, XRD studies were carried out. Fig. 3, shows the XRD patterns of GO, RGO, PRGO and PHG nano-structured composite hydrogels. GO consists a sharp peak at $2\theta = 12^\circ$ ($d = 7.374 \text{ \AA}$), while peak at 25.6° ($d = 3.479 \text{ \AA}$) in RGO confirms the reduction of GO through hydrazine hydrate to produce reduced graphene oxide²⁴.

The characteristic diffraction peaks of PANi centred at 2θ values of 20.1° due to the crystallinity and the aligned polymer chains²⁵ and 25.4° corresponding to the periodic $\pi - \pi$ stacking of the polymer chains²⁶.

XRD results illustrate the crystal structure of the PRGO composite hydrogel with the two individual constituents in the composite hydrogel. As can be seen from the XRD plots, that no extra peak appears in the as-synthesized composite, implying that is only the substitution of RGO in polyaniline hydrogel takes place rather than any chemical reaction taking place.

b. SEM Analysis

SEM technique has been employed to have an insight into themorphology and structure of these hydrogels. As can be seen in Fig. 4, the hydrogel is composed of small platelets of polyaniline struck on each other, and some granular particles appear on the surface. SEM image further reveals the presence of RGO within the polymer network matrix. 3D mesh-like network of polyaniline hydrogel is induced due to the phytic acid acting as cross-linkers. Since, phytic acid molecules interact with various polyaniline chains, lead to cross-linked structure with higher effective surface area and increased transport of charge carriers. Furthermore, porous structure of hydrogel and the availability of excess of water, it

develops additional surface area between the solution phase and polyaniline chains.

c. Electrochemical Characterization

The estimation of electrochemical properties of PHG and PRGO was carried out in a two electrode cell by placing Whatman filter paper as a separator between symmetrical polyaniline hydrogels coated carbon cloth electrodes using 1M H₂SO₄ aqueous electrolyte. The nature of electrochemical processes occurring at the interface of an electrochemical cell is reflected in the cyclic voltammetry (CV) profile. Due to the insitu growth of composite hydrogel on carbon cloth, there is a significant enhancement occurring in the CV integrated area corresponding to a high specific capacitance. Fig. 5(A) represents the CV graphs of pure PANi/HG@cc and PRGO composite hydrogel based capacitor cells 1M H₂SO₄ aqueous electrolyte with potential window -0.2 V to 0.8 V at a scan rate of 20 mV/s. The CV curves of PANi-hydrogel and PRGO composite hydrogel-based capacitor cells exhibit two pairs of redox peaks that can be assigned to the leucoemeraldine to emeraldine and emeraldine to pernigraniline transitions of polyaniline⁶. It is important to note that the PRGO nano-structured composite as an electrode material shows the highest current density, indicating its high capacitive performance. Due to unique structure and synergistic effects between the two components, an improved electrochemical performance of PRGO hydrogel has been achieved. The presence of RGO seems to improve the conductivity as well as manage the morphology thereby assisting in high rates of electrode reaction and high electrode/electrolyte contact areas, evolving in improved electrochemical performance. Also, the overall capacitance was significantly enhanced by the pseudo-capacitance properties of polyaniline. The specific capacitance of PANi hydrogel @ carbon cloth and PRGO composite hydrogel @ carbon cloth based capacitor cells were evaluated from the CV profile using equation²⁷.

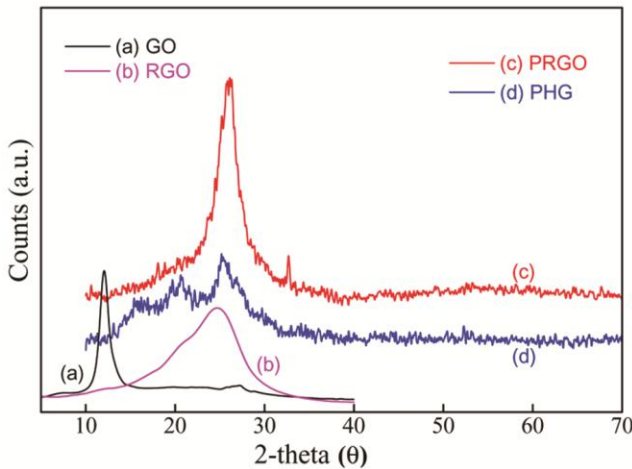


Fig. 3 — X-ray diffraction patterns of the as-prepared samples (a) GO, (b) RGO, (c) PRGO and (d) PHG.

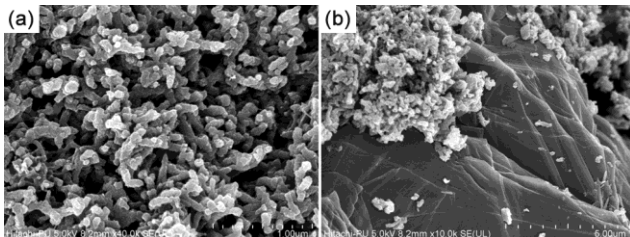


Fig. 4 — SEM images of the as-prepared (a) PHG and (b) PRGO composite hydrogel.

$$C_s = \frac{1}{m \cdot \Delta V \cdot s} \int I(V) \cdot dV \quad \dots (1)$$

where *s* is the scan rate, Δ*V* is the potential window, *m* is the mass of single electrode, and ∫ *I(V) · dV* is the integrated area of the CV curve. The specific capacitance values so obtained are comparable to the values attained from charge-discharge analysis.

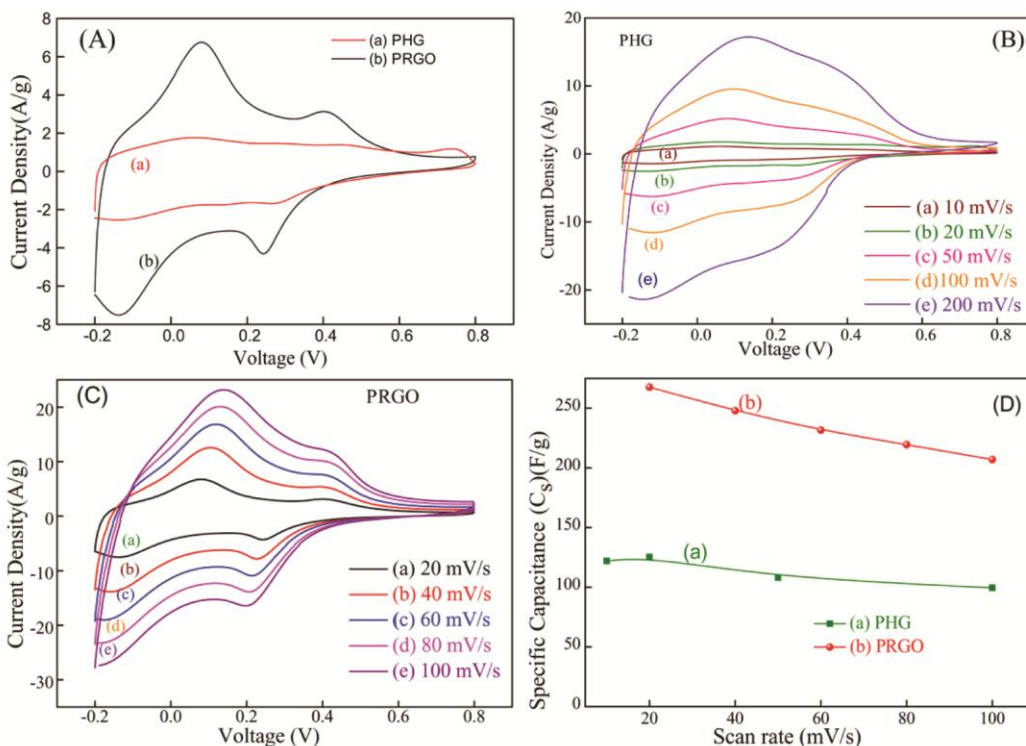


Fig. 5 — (A) CV plots of PHG and PRGO hydrogel based cell at 20 mVs⁻¹. (B) CV plots of PHG composite hydrogel based cells at different scan rates. (C) CV plots of pure PRGO hydrogel based cell at different scan rates. (D) The dependence of specific capacitance of cells on scan rate for (a) PHG and (b) PRGO composite hydrogel.

Figs. 5(B-C) depict the CV curves of pure PHG and PRGO composite hydrogel based capacitor cells at different scan rates with potential window -0.2 V to 0.8 V in 1M H₂SO₄ aqueous electrolyte. It is well known that the current density expands with the scan rate due to an increase in electron transportation, illustrating the high rate property and superb capacitive behaviour. The CV curves reveal that as the scan rate increases, correspondingly specific capacitance decreases, which may be due to the increase in the ionic diffusion resistance. The variation in the specific capacitance of the capacitor cells (PHG and PRGO composite hydrogel) with distinct scan rates is shown in Fig. 5(D). Highest C_s value of 267.63 F/g at a scan rate of 20 mV/s has been recorded for PRGO composite @ carbon cloth electrode and found to decrease with the increasing scan rate. It may be attributed as diffusion limit of the electrolyte ions. At lower scan rate, ions have sufficient time to penetrate and interact with larger surface area of the electrode material resulting in higher value C_s. Effectively, the binder free preparation of electrode and the porous morphology of PRGO hydrogel improves the value of C_s.

Galvanostatic charge discharge (GCD) is a significant method to characterize the performance of a capacitor cell. The GCD measurements were carried out at 0.25–7.5 A/g in a potential window between 0 and 0.8 V. The discharging behaviour shows a sudden IR voltage drop and then a slow decay of voltage. The IR drop accounts for the internal resistance of electrode. The specific capacitance was estimated from the GCD plots according to the equation²⁸.

$$C_s = \frac{I * t_d}{m * \Delta V} \quad \dots (2)$$

where, m is the mass of each electrode, I is the applied current, ΔV is the potential window and t_d is the discharging time. The PRGO composite hydrogel @ carbon cloth electrode-based capacitor cell shows the highest C_s value of 235.32 F/g. Similar to the CV measurements, the PRGO composite hydrogel electrode-based cell showed high specific capacitance than the pure PRGO based cell. The electrochemical behaviour of PRGO@ carbon cloth electrode was investigated at different current densities and at various scan rates the results are listed in Table 1.

The galvanostatic charge-discharge plots of PRGO composite hydrogel electrode based capacitor cell at different current density range were analysed and the variation of the specific capacitance with the current density is plotted in Fig. 6(A). The inset reveals the galvanostatic charge/discharge curves of PRGO composite hydrogel-based cell at different current densities. As the current densities increase the time duration decreases, however the charge/discharge (CD) curves maintain a similar shape, showing the sustainable behaviour of the composite hydrogel. Cycling performance is also a significant factor in analysing the electrochemical performance of electrodes for practical applications. Cycle stability of the PRGO composite hydrogel electrode based capacitor cell was examined at a current density of 1 A/g (Fig. 6B). After 1000 cycles, the PRGO composite hydrogel electrode-based capacitor cell retained about 92% of initial capacitance, showing superior capability of reversibility in consecutive charge/discharge cycles.

The good stability of PRGO composite hydrogel electrode based capacitor cell may be ascribed to the synergistic effects among the two components of the composite and the well-designed nano-structure. PANi

alone is a pseudo capacitor electrode material that exhibits reduced cycling stability, the incorporation of RGO sheets can effectively prevent the shrinkage and swelling of polyaniline during doping/de-doping procedures, thus the composite material turn out to be more valuable against volumetric variation through redox reaction. PRGO composite hydrogel indicated excellent rate capability because of the good contact between, polyaniline, RGO and carbon cloth.

The highest measured C_s is ~136.55 F/g for the PHG based capacitor cell and ~235.32 F/g for the PRGO composite hydrogel-based capacitor cell with a loading of 10 wt.% RGO. The greater specific capacitance for PRGO composite hydrogel originates from two different charge storage processes: (1) the EDLC storage mechanism in RGO (2) the surface pseudo-capacitance behaviour of the polyaniline. The incorporation of RGO in polymer matrix improves the electrical conductivity resulting in high C_s value of 235.32 F/g was obtained for PRGO composite hydrogel. The other parameters that are power and energy density have also been calculated using following equations^{29,30}

$$E = \frac{1}{2M} C_{cell} V^2 \quad \dots (3)$$

$$P = \frac{V^2}{4M \times ESR} \quad \dots (4)$$

Table 1 — Specific capacitance from CV and GCD for the PRGO composite hydrogel electrode-based capacitor cell.

CV		GCD	
Scan rate (mV/s)	C_s (F/g)	Current density (A/g)	C_s (F/g)
20	267.63	0.25	235.32
40	247.91	0.5	234.29
60	231.60	1	241.44
80	219.53	5	232.58
100	207	7.5	229

Where, M is the mass of both the capacitor electrodes and V is the voltage exclusive of the equivalent series internal resistance (ESR). The PRGO composite hydrogel electrode-based capacitor cell revealed high power and energy density (151 W/kg & 3.9922 Wh/kg) as compared to pristine PHG (48.55 W/kg & 1.6 Wh/kg). Hence the electrochemical

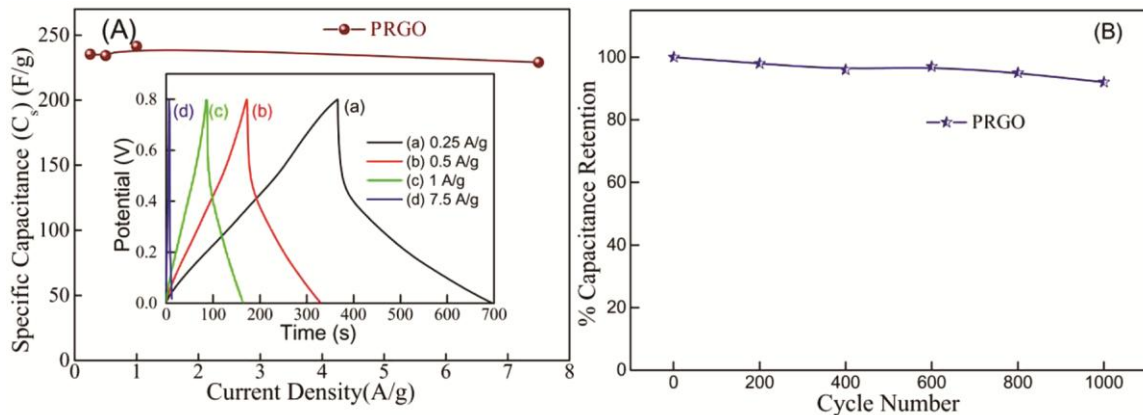


Fig. 6 — (A) Variation of the specific capacitance of PRGO hydrogel, the inset depicts GCD plots of PRGO hydrogel at various current densities.(B) Cycle stability of PRGO hydrogel at a current density of 1 A/g for long-standing charging/discharging process.

results show that the conducting polymer based composite hydrogel is a favourable candidate for the supercapacitors with a high value of specific capacitance.

4 Conclusion

A facile and scalable phytic acid-mediated synthesis route has been employed to fabricate a highly porous 3D nano-structured conductive hydrogel with improved electrochemical activity and electrical conductivity. Phytic acid (PA) acts as a good medium for the dispersion of reduced graphene oxide in aqueous solution, an excellent gelator/dopant to produce cross-linked structure of polyaniline chains into hydrogels. The growth of polyaniline onto the surface of RGO sheets and hence on carbon cloth, leads to the formation of PRGO composite hydrogel. The as-synthesized 3D conductive network has directional passages for efficient charge transport and high surface area. The composite hydrogel electrode on carbon cloth yields high electrochemical capacitance due to extended faradaic interaction sites for the hybrid supercapacitor electrode. The results indicate that the PRGO composite hydrogel possesses superior electrochemical capability with a high C_s value of 235.32 F/g. Thus, the phytic acid-arbitrated polyaniline reduced graphene oxide composite hydrogel electrodes open a low-cost route for mass-scale manufacture of electrodes for supercapacitor applications.

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