Sustainable approach for reclamation of graphite from spent lithium-ion batteries

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Abstract
A scalable and facile regeneration route is utilized to recover the graphite from a spent lithium-ion battery (LIB). Eco-friendly organic acid is employed as a leaching-curing reagent for the present work. All the unwanted content of elements e.g. Ni, Co, Li, Cu and Al has been completely terminated from the graphite after the purification step without any additional calcination process. The optical, structural and electrochemical properties of as-reclaimed graphite have been studied by several analytical methods. Regenerated graphite is restored to its layered crystal structure along with expansion in the interlayer distance, and the same is confirmed from scanning electron microscopy and X-ray diffraction analysis respectively. Notably, high purity graphite is achieved and tested in its electrochemical storage property in supercapacitor (SC) applications. As an outcome, recreated graphite exhibits a maximum areal capacitance of 285 mF cm$^{-2}$ at 5 mV s$^{-1}$.

The fabricated symmetric SC demonstrates the superior energy storage performance in terms of durability and higher capacitance (131 mF cm$^{-2}$) with better capacity retention over several cycles. It is worth mentioning that this curing process is a facile route, consumes lower energy and eco-friendly methodology and thereby may have futuristic extent for the bench scale reclamation of graphite from spent LIBs.

1. Introduction

Over the past few decades, lithium ion batteries (LIBs) have been widely used in several consumer electronic devices such as laptops, computers, mobile phones and especially higher energy density applications including electric vehicles, hybrid electric vehicles and plug in vehicles [1, 2]. This indicates that the production and applicability of LIBs towards energy storage systems are continuously rising, while at the same time overloading of multiple elements causes scarcity in future and substantial generation of spent LIBs. The projected value of spent LIBs is close to 11 million tonnes in the year 2030 and even more possibilities with an implementation goal towards net zero emission of green house gases [3, 4]. The LIBs consist of non eco-friendly electrolyte materials and heavy transition metals form the electrodes. As a result of this, extra burden is paid to the crucial electrode/electrolyte raw resources leading to increase in cost of the device [1–5]. Based on these attributives and significant quantities of metals/materials, the recycling of spent LIB strategies have been emerged recently in order to save the valuable materials and also development of sustainable environment as well as creation of greener energy technology. It is really worth to note that, the re-creation of spent materials into valuable product provides an economical benefits as well as mitigating the environmental hazards. Hence, regeneration of spent material is one of the alternate and key research directions towards development of sustainable energy growth and circular economy [6].

Generally, LIB contains three fundamental parts such as anode, cathode and electrolyte, and commercially manufactured in variety of shapes, sizes and designs. Mostly, graphite is used as the anode material whereas cathode materials are Li-metal oxides and its derivatives and phosphides, etc. The transport of Li$^+$ between anode to cathode and vice-versa takes place through electrolytes (organic, and polymer
electrolytes, etc) [7, 8]. An ample of attempt has been carried out by the scientific community towards the recycling technology of spent LIBs in order to recover the valuable heavy metals, from cathode part because it contains numerous critical elements including Li, Co, Ni, Mn, Al etc [3, 6, 9]. Several metallurgical methods and novel investigations such as pyro, hydro and bio-metallurgical process, combined metallurgical route and cost-effective ideas have been implemented to recover valuable metals. Only a very few investigations report on the recovery of graphite/anode compared to Li, Co, Mn and Ni recovery from cathode [9]. It might be an inappropriate presumption that graphite is a low-cost material and available plenty in earth's crust and it can be directly land filled or incinerated [3]. A noteworthy observation, increasing the usage and production of LIBs leads to expanding the consumption of graphite resources. This will definitely increase the price of the graphite and reduces its abundance on earth's crust. In addition, available graphite content in LIBs nearly ranges between 12%–21% and the cost of the 1 ton spent LIBs is around $7708 in which graphite cost is $170 [10]. Based on the reports of royal society of chemistry (RSC) and joint research centre (JRC) analysis, the graphite material has been categorized as the level of higher medium and the supply risk index of 8.1 [11–13]. Therefore, regeneration of graphite from spent storage devices holds an excellent future along with waste to wealth technology, sustainable living and mitigates the environmental hazards.

In the present work, restoration of graphite has been demonstrated by hydrometallurgical route and employing organic acid as a curing reagent. According to the reclamation methodologies, several chemical reagents have been utilized and are inorganic acids, organic acids and ammonia related chemicals [4]. Among them, organic acid adapted reclamation route provides an extra advantages such as environmental friendly, absence of evolving dangerous gases during leaching/curing process, higher efficiency and cost-economics [14, 15]. Mostly, organic acid assisted regeneration process focused to recover the selective metal species from cathode part. There is no work has been reported on the recovery of anode part. Herein, authors have attempted for the first time to recover the graphite from spent batteries using acetic acid as a reagent. The following literature supports worth of graphite generation from spent LIBs by several strategies and the present work is entirely distinct from that reported in literature. For instance, Xiaotu et al [7] has investigated the purification of spent graphite by hydrometallurgical process using H$_2$SO$_4$ and H$_2$O$_2$ as an oxidizing and reducing agents. The recycled graphite consists of un-dissolved impurities, hence it is un-utilizable further. Therefore, authors have again performed the leaching process along with inclusion of fusion agents in order to reduce the impurities associated with the recycled graphite. From the results, purified graphite is free from impurity and proficient to serve as an anode material for LIBs. Finally, test result shows the capacity of 377.3 mA h g$^{-1}$ at 0.1 C rate which is higher than the theoretical specific capacity (372 mA h g$^{-1}$).

On the one hand, Gao et al [2] reported the regeneration of graphite from spent LIBs via combination of H$_2$SO$_4$ curing-leaching process and followed by high temperature calcination. The morphological and structural properties of recycled graphite are examined by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Raman analysis. The surface morphology of the recycled graphite is turned into homogeneous and smooth after the calcination process. Almost all the impurities in the used graphite are reduced significantly after the curing-leaching phenomena thereby able to attain higher grade graphite. As a whole, the regenerated graphite demonstrated better electrochemical properties in terms of capacity and rate capability. Recently, electrolysis process and mechanical crushing with the pyrolysis-flotation method is applied to recover the graphite, studied by Ning Cao [8] and Zhang et al respectively [16]. However, these recovery methods are limited with the involvement of several preparation steps and complexed experimental methodology as well. Hence, implementations of economic as well as facile preparation routes are highly demanded and welcomed step towards anode recovery in a more sustainable and cost-effective way.

With this perspective, mild acetic acid curing route is adopted and potentially reclaimed the graphite without any foreign metals. Prior to curing process, the pretreatment, dismantling and sieving have been carried out. Then, the separated graphite from Cu-metallic foil is used for the further experiments. Acetic acid supported leaching process effectively reduces the impurities associated with the untreated graphite. Finally, cured graphite has been analyzed their structural, optical, morphological and electrochemical properties using XRD, Raman spectroscopy, SEM and cyclic voltammetry (CV) and galvanostatic charging/discharging (GCD) analysis, respectively. By this process, restored graphite demonstrated an excellent electrochemical property and can be used as anode material for supercapacitors (SCs), Al-ion batteries, Li-ion batteries, K-ion batteries, and Na-ion batteries. Herein, reclaimed graphite is tested and applied for the SC operations.

More interestingly, impact of binder on the electrochemical properties of regenerated graphite material is investigated for the first time with use of polystyrene sponge foam. In all the energy storage devices, binder material plays a dominant role in connecting the active material, carbon black and current collectors. Also, supplies the favorable electrical framework to activate good transportation of ions as well as maintains the electrical conduction and structural integrity in the respective electrode. Normally, several attempts has already been implemented to study the electrochemical performance of electrode materials with an
adaptation of polyvinyl alcohol (PVA), poly(methyl methacrylate), and carboxymethyl cellulose, etc has been used as a binder compounds [17, 18]. In the present work, waste polystyrene foam is utilized as the binder material towards the graphite based SC applications. Importantly, these polystyrene based polymeric materials/substrates are majorly responsible for the plastic pollution [19]. This may be because of their non-degradable nature as well as sources for the creation of micro plastics [20, 21]. In combo process of recycling technology and waste polystyrene plastic foam utilization obviously leads to environmental mitigation by designing pollution free greener carbon compounds from the spent devices. Finally, symmetric SC is assembled using the regenerated graphite sample, tested and their electrochemical evaluation is discussed. The fabricated SSC device shows the maximized areal capacitance of 131 mF cm\(^{-2}\) for RG with polyvinylidene fluoride (PVdF) used binder.

2. Experimental section

2.1. Materials

The multi varieties of spent LIBs were purchased from local electrical markets in Bhubaneswar, Odisha-India. All the reagents were bought from analytical grades and used without any further purification. The acetic acid with purity of 98% was purchased from Rankem Pvt. Ltd. De-mineralized water was used for the washing and cleaning process. The sodium chloride (NaCl) was purchased from SRL Chemicals Pvt. Ltd, India. The binder PVdF, carbon black and N-Methyl-pyrrolidone were purchased from Sigma–Aldrich.

2.2. Experimental and characterization methods

First step of regeneration route is pretreatment and followed by dismantling, crushing and separation process. Before to the pretreatment process, collected LIBs were soaked in 5% NaCl solution over-night in order to reach fully discharged state to avoid short circuit and any flammable issues during the manual dismantling process. Thereafter, the collected LIBs were dismantled manually and the anode current collector was separated from the battery case. The graphite powder was scrapped from Cu-current collector and used in the curing experiments. In this work, spent graphite was collected from several batteries. The required amount of collected graphite powder was properly mixed with a solvent contains 30% acetic acid and 70% de-mineralized water, stirred for 6 h at 80 °C. The experiments were repeated twice in order to terminate the heavy metal impurities from the spent graphite. The filtered solution was stored for the analysis and graphite was obtained in the form of filter cake. Finally, the filtered graphite residue was dried at 80 °C and stored for physical and electrochemical studies.

The impurity solubilization in filtered solution was studied by atomic absorption spectroscopy (AAS) and inductively-coupled plasma- optical emission spectroscopy (ICP-OES-Thermo Scientific, iCAP 7000 series) analysis. After the second curing process, almost all the impurities were entirely dissolved in the acidic media thereby pure regenerated graphite was obtained. The structural and optical properties of regenerated graphite samples were studied by XRD (Siemens D5000 X-ray diffractometer) and Raman (Renishaw plc, Gloucestershire) analysis. The morphological and elemental energy dispersive X-ray analysis (EDX) properties of untreated and reclaimed graphite samples were performed using SEM (Carl ZEISS-EVO-18). Furthermore, lattice and selected area electron diffraction (SAED) pattern of graphite was evaluated by transmission electron microscopy (TEM) analysis using Carl-ZEISS model. The electrochemical properties of restored graphite were analyzed by CV and GCD analysis with the help of Bio-Logic-SP-200 instrument.

The 1 M potassium hydroxide (KOH) solution was used as the aqueous electrolyte whereas Ag/AgCl, Pt-wire and graphite coated Ni-foam were used as the reference, counter and working electrodes, respectively. For the slurry preparation, 85 wt% regenerated graphite, 5 wt% PVdF, and 10 wt% carbon black were properly mixed using N-methyl pyrrolidone as a solvent, which noted as active material. The active material was coated on the Ni-foam and dried at 80 °C in an oven.

Prior to coating process, Ni-foam was fully cleaned with acid, water and acetone and allowed it to dry in an oven for 1 h. For the fabrication of a symmetric SC, similar amount of active materials was coated on the Cu-plate. The PVA-KOH gel polymer electrolyte (GPE) was prepared and used as the electrolyte for the symmetric SC (SSC). For the preparation of GPE, fixed amount of PVA-KOH was dispersed in the 50 ml of de-mineralized water and stirred at 80 °C until the gel was formed. The normal filter paper was utilized as a separator for the SC assembly. The geometry of the assembled storage device was explained in the results and discussion section. Investigation on electrochemical activities of assembled SC was studied with the help of CV and GCD studies over several sweep rates and specific current densities respectively. Electrochemical impedance analysis (EIS) also carried out in order to analyze the compatibility between electrode/electrolyte boundary and charge transfer resistance of the same. Furthermore, cycling stability of the symmetric SC was performed over many cycles. It may be noted that, effective role of binder on the electrochemical properties of graphite was studied in the present investigation. For this, waste polystyrene sponge-foam material was
used for the slurry preparation instead of that PVdF binder without any purification treatment. The photograph of the foam is shown in the figure 1(a). Thus, it proves that the implementation of cost-effective strategy for graphite utilization towards the energy storage is possible. In this study, the electrochemical parameters were compared and discussed.

3. Results and discussion

3.1. Structural analysis

The first and second curing filtrate solution has been analyzed by ICP-OES & AAS analysis. The obtained content of elements during curing phenomena is quantitatively given in figure 1(b), which reveals that the amount of all impurity elements is removed entirely from the graphite. The result is further consistent with the following analysis and discussion. For the comparison purpose, the physicochemical properties of the untreated, commercial and regenerated graphite have been analyzed by several analytical techniques and are designated as UG, CG and RG respectively. Figure 2(a) portrays the XRD patterns of RG, CG and UG at ambient temperature. It can be seen from figure 2(a), all the samples (i.e. commercial and regenerated) show strong and sharp diffracted peak, which revealing the existence of purity in RG. The peak monitored around $2\theta = 26.4^\circ$ which is attributed to the characteristic peak of the graphite and corresponds to the (002) plane. The diffraction peaks for all the graphite samples are perfectly matched and indexed with the standard JCPDS diffraction pattern (Card No.: 41-1487) with space group of P63/mmc. Thus, it proves the structure of graphite remains similar without any noticeable changes after the acetic acid treatment except the lattice d-spacing. The stronger diffracted peak has been shifted to lower angle ($26.4^\circ$) when compared to UG ($26.5^\circ$) which may be due to increment in the interlayer distance of the graphite [22]. Also, major peak of UG is slightly asymmetric which might be attributed to the changes in the crystal orientation of lattice point and repeated insertion of Li-ions when LIBs in an operational condition. After the acetic acid treatment, the graphite crystal structure has been regained when compared to CG via appearance of symmetrical peak with higher inter layer spacing. The enlarged view is shown in figure 2(b).

Furthermore, no observed peaks correspond to the other metal elements and binder compounds that validates worth of the curing process and absolutely terminating the impurity elements in the graphite. The interlayer distance of reclaimed graphite is higher than that of untreated sample and the estimated d-spacing values are 0.336 nm and 0.337 nm for UG and RG sample respectively, which is perfectly indexed with the reported survey of regenerated graphite from spent devices [23]. In other words, the enriched interlayer distance is ascribed to the co-intercalation of solvated Li-ions as well as co-infusion of impurities and electrolyte decomposition as the initial formation of solid electrolyte interface (SEI) [23, 24].

A further confirmation of purity and crystal structure of graphite, Rietveld refinement has been performed and their results are given in figure 2(c). Refined pattern ensures that the acid treated graphite shows hexagonal structure with well crystalline and sharp diffracted peaks. From the Rietveld results, accurate lattice values are evaluated and are $a = 24.62$ nm, $b = 24.62$ nm and $c = 67.08$ nm and $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$. The reliability parameters such as $\psi^2$, $R_p$ and $R_{wp}$ are found to be 8.7%, 9.3% and 14.4%.
respectively. In addition to that, hexagonal crystal symmetry is additionally validated by generated crystal structure of graphite with help of Vesta platform and its image is depicted in figure 2(d). Noteworthy, crystal structure and surface morphology of the graphite is not altered after the multiple charging/discharging processes of Li\(^+\). Thereby, maintaining the structure as well as layered morphology in acid treated sample, which confirms the significance of graphite reclamation from spent LIBs and same is again judged by SEM analysis. Also, reclaimed graphite is free from impurities and can be used as an anode material for several forthcoming energy storage devices. Moreover, the effect of purification is further validated by the crystallinity calculation. The crystallinity value of recovered graphite is 52 ± 0.25% which is superior to the commercial graphite (47 ± 0.28%) value.

3.2. Mechanism of curing process using acetic acid
According to crystal symmetry and structure of graphite, Li-ions are intercalated into layered structure when charging and de-intercalated while discharging. A few irreversible Li-ions are stuck in layered structure and react with the liquid electrolyte thereby formation of SEI. Notably, some content of the transition metal elements also probably exists in the anode part, which may be due to manual dismantling, separation process and complex electrochemistry of the spent device. Hence, in order to remove the impurities, SEI and organic compounds, several efforts have been made. Herein, combo of mild acetic acid and water is selected as a curing reagent and graphic of curing mechanism is illustrated in figure 3. The collected Cu-foil with graphite material has been separated and it consists of Cu, Al, Fe, Co, Li and Ni. Normally, irreversible Li\(^+\) and non-conductive metal impurity in graphite host react with water and acetic acid, which leads to production of acetate ions and hydronium ions. This can dissolve the metal impurities and water soluble lithium products thereby attaining impurity-free graphite with a larger inter-planer value, which encourages the electrochemical activity of graphite via restoration of the conducting channels. Here, all metal impurities are allowed to the solubilization process rather than the leaching process. Moreover, there is no evolution of toxic

![Figure 2. (a) XRD pattern of different graphite samples (b) enlarged peak position of (002) plane of different graphite samples (c) Rietveld XRD pattern of RG (blue lines indicates difference in observed and calculated ones, and green peaks shows diffracted peak) (d) refined crystal structure of RG.](image-url)
gases in the present organic acid curing treatment. At higher temperature reaction promotes the curing reaction and permits more proton-ions to interact with the graphite thereby dominates the metal dissolution process. Overall, the contribution of acetic acid and water helps to remodel the crystal structure of graphite and strongly decomposes the non-conducting metal elements.

As a matter of fact, Li-depletion takes place initially then followed by recombination of electron within particle leads to reduce the excess metal elements. Moreover, the exchange of proton and Li-ions are simultaneously occurred in the solubilization process [25, 26]. The highlighted curing process is due to the greater concentration of H-ions and mainly depends on the nature of the acid as well as chemical composition. Thereby, rate of the cleaning process is accelerated to a greater extent. However, detailed understanding of leaching/curing process is unclear and need to be researched further and rarely being reported. For instance, simple water treatment-assisted graphite reclamation has been executed by Wang et al [23]. As per their approach, removal of foreign elements and separation of SEI in spent graphite takes place through the generation of H₂ gas. On the other hand, citric acid supported curing/leaching process of graphite is studied by Yang et al [27]. The presence of tricarboxylic acid with the multiple H⁺ ionization leads to formation of lithium citrate product and remaining metal impurities are dissolved in the acid solution.

3.3. Raman analysis
The Raman spectra of UG, RG and CG are given in the figure 4 with wavenumber ranges from 500 to 3500 cm⁻¹. As noticed from figure 4, all the samples demonstrate three stronger vibrational peaks and one shoulder peak. The stronger vibrational band is observed at 1355 cm⁻¹ for RG sample and is ascribed to the D-band which means that lattice defects in the carbon atoms. This band has been shifted to the lower wavenumber for other graphite samples (1353 cm⁻¹ for CG and 1351 cm⁻¹ for UG). Another more prominent band located at 1582 cm⁻¹ which is attributed to the G-band (graphitization) and indicates that the in-plane stretching mode of sp² carbon [22–24, 28]. This G-band stretching mode has been migrated to 1580 cm⁻¹ for UG and 1581 cm⁻¹ for CG sample. The intensity value of \( \frac{I_D}{I_G} \) is suggesting that unveiling defect concentration in the structure of graphite. As calculated \( \frac{I_D}{I_G} \) ratio for RG sample is 0.20 and same is well accordance with the reported survey [29]. The other graphite samples show an intensity ratio of 0.37 and 0.24 for UG and CG respectively. Evidently, the prevailing graphitization degree is demonstrated by reclaimed graphite when compared to both UG and CG.

The weak band monitored at wavenumber 2451, 2458 & 2453 for the UG, CG and RG material and corresponds to the vibrational stretching band of D + D'' [30]. It is important to note that, another major
band is observed at 2720 cm\(^{-1}\) for RG which is due to two times D-band (2D) in the carbon atoms \([30]\) i.e. production of two phonons with inverse momentum and results in the double resonance transitions. This band has been designated as a special sign for the graphitic carbon \([31]\). Normally, the presence of 2D band confirms the persistence of graphite in as-reclaimed material \([3]\). The 2D band has been shifted to the 2715 and 2714 cm\(^{-1}\) for CG and UG. Raman analysis obviously endorse that the regenerated graphite material is free from metal and metal oxide related vibrational bands.

### 3.4. Morphological analysis

The surface micrographs of untreated, regenerated and commercial graphite samples are portrayed in the figures 5(a)–(c). The untreated graphite shows the smooth and disordered flake particles combined to appear like spherical type micro grains. Whereas acetic acid assisted graphite sample reveals the unwrinkled and intact micro-sized aggregated flake particles are unanimously allocated over the surface. For the morphological comparison, there is not much discrepancy exist between treated and untreated graphite micro-particles which means that surface morphology of the same is not influenced by multi-times charging/discharging and reclamation process as well \([7]\). Both the graphite (UG and RG) samples demonstrate the aggregated spherical shaped flake micro grains and are inherently connected to form a large block like graphite network. Notably, untreated and acetic acid assisted regenerated graphite still retains the layered surface morphology and same is shown as inset of the respective micrographs (figures 5(a) and (b)). The observed morphology of both UG and RG is consistent with the CG morphology. The CG also clearly indicates the graphite micro grains are distributed over surface with uniform nature (figure 5(c)). On the one hand, untreated graphite sample contains numerous metal impurities such as Ni, Co, Cu, Al & Fe whereas reclaimed graphite is entirely free from impurities, which is additionally ascertained the obtained results from AAS and ICP-OES analysis.

The EDAX results of the all graphite systems is given in the figures 5(d)–(f). The elemental percentage of UG, RG and CG are listed in the table 1. From the EDAX spectrum, the carbon peak in RG sample is more dominant and stronger after the acetic acid curing process which indicates that the all metal impurities are terminated from the graphite (figure 5(e)). The employment of organic acid eliminates the problem of waste water and environmental issues. Hence, this organic acid based curing—leaching process is an eco-friendly and economical trend to regenerate the spent graphite into valuable products. However, CG contains small amount of oxygen moieties and the percentage of the same is found in table 1.
In order to support the observed spherical morphology of RG from SEM results, TEM analysis has been performed and its results are portrayed in figure 6. As seen in figures 6(a) and (b) confirmation of spherical type micro graphite particles with excellent packing density is revealed. In addition, layered structure of graphite is evidently observed with free from impurities and by-products while regeneration or curing process of UG and shown in figure 6(c). The calculated lattice d-spacing of 0.337 nm for the (002) plane from XRD analysis is perfectly accordance with the TEM lattice fringe patterns, as given in figure 6(d). This result further supports the worth of curing process of UG and enlarged lattice interlayer value is highly

| Elements | UG Normal wt % | Atomic % | RG Normal wt % | Atomic % | CG Normal wt % | Atomic % |
|----------|----------------|----------|----------------|----------|----------------|----------|
| C        | 86.17          | 90.73    | 100            | 100      | 96.92          | 97.67    |
| O        | 10.95          | 8.65     |                |          | 3.08           | 2.33     |
| Co       | 0.26           | 0.05     |                |          |                |          |
| Cu       | 2.18           | 0.43     |                |          |                |          |
| Ni       | 0.3            | 0.06     |                |          |                |          |
| Al       | 0.15           | 0.07     |                |          |                |          |
beneficial to act as active sites for the greater storage of ions. The higher d-spacing is mainly due to continuous intercalation and de-intercalation of Li\(^+\) among metal oxide and graphite layers.

Particle size determination measurement also one of the well-known technique to determine the parameter and quality of the recovered product. The average particle sizes of all the graphite samples are found to be similar range. More specifically, average graphite particle size of 19.63 µm is forecasted for RG after regeneration process whereas spent graphite shows the value of 21.82 µm. This result is nearly equal to the commercial graphite value and the value is found to be 24.1 µm. The recovered graphite exhibits the good physicochemical properties when compared to commercial graphite. On the other hand, CHNSO analysis has been performed to support the curing process of UG. After the acetic acid treatment, carbon content has improved been greater level and the value is 99.4% which is higher than the spent graphite (87.6%). This is ascribed to the reclamation of ordered and layered structure of graphite with excellent purity.

3.5. Electrochemical studies
3.5.1. CV analysis
The energy storage evaluation of regenerated and commercial graphite has been examined by CV and GCD analysis using conventional three-electrode systems. As mentioned in the experimental section, the polystyrene foam material is used as a binder and impact of the same on the energy storage activity of both the graphite materials have been investigated in the present work. Figure 7 shows the CV profile for regenerated and commercial graphite samples with multiple sweep rates starting from 5 to 100 mV s\(^{-1}\). The voltage range between 0.3 to \(-0.4\) V is selected as the potential window for the present investigation. More interestingly, both the binder i.e. waste sponge and PVdF utilized graphite anode samples exhibit electrical double layer capacitor (EDLC) property without any redox activities. Both the RG and CG material undergoes the non-Faradaic charge storage mechanism. In other words, surface charge generation has been induced by the dissociation of active electrode surface as well as adsorption of ions in the electrolytes electro-statically [32].

The CV plots correspond to the both foam and PVdF binder used RG and CG samples display the similar EDLC behavior, which validates the regenerated graphite does not lose its electrochemical nature when compared to commercial graphite. At the same time, CG with foam behaves quite distinct nature due to interaction between electrode and electrolyte medium. This interaction highly influences the work function.
of the graphite material and results in the alternation in the nature of the conducting mechanism and potential window as well as cycling behavior \[33, 34\].

RG sample is found to be delivering the superior electrochemical performance than that of commercial graphite. This may be ascribed to the effect of various functional groups that are present in the PVdF macromolecular backbone and also enriched inter-lattice spacing of RG, which assist the insertion of more cations in a reversible manner, thus increases the contact among electrode material. Binder material can act as an electrical network among active sample and carbon black, also influences the electronic transportation to certain extent \[17, 18\]. This phenomenon is occurring via reducing the crack or voids formation in the active electrode, thereby able to obtain overwhelmed storage performance. Notably, area of the CV curve seems to be increased with increasing the sweep rates from 5 to 100 mV s\(^{-1}\) for both RG and CG samples indicating the capacitance behavior and better rate properties. The areal capacitance of active electrode material is estimated from CV plots by using the formula \[35\],

\[
C_{ap} = \frac{\int i(\nu) \, d\nu}{A \times R \times \Delta \nu} \tag{1}
\]

where \(\int i(\nu) \, d\nu\) is the area under the CV plot, \(A\) is the area of the active electrode (cm\(^2\)), \(R\) is the sweep rate and \(\Delta \nu\) is the window potential of CV plot.

Figure 8 shows the compared areal capacitance versus sweep rates for all the graphite samples. A noteworthy observation from all the graphite samples, lower sweep rate shows the higher areal capacitance values which may be due to the faster movement of electrolyte cations and makes the better interaction among graphite particles. In other words, electrolyte ion has enough time to engage wider space in the active graphite sample and provides supreme pathways for the migration of ions via greater electroactive sites at lower sweep rate \[32\]. As an outcome, PVdF assisted RG sample shows the maximum areal capacitance of 285 mF cm\(^{-2}\) at 5 mV s\(^{-1}\) whereas polystyrene foam used RG displays lower capacitance and the value found to be 179 mF cm\(^{-2}\) at the same scan rate. Importantly, both the RG and CG samples show the similar lattice d-space values but significant storage behavior is noticed for RG in terms of higher current. Apart from lattice d-space, more critical factors responsible for the good electrochemical performance includes good

![Figure 7. CV plots of (a) RG with PVdF (b) RG with Foam (c) CG with PVdF (d) CG with Foam.](image-url)
conducting pathways for ions, particle size and crystallite size, constructive electroactive sites, better interaction of active electrode and electrolyte medium, etc. For instance, Chenxing et al [36] have examined the energy storage performance of regenerated graphite with different mesh size and a significant deviation in the electrochemical performance is observed. This different electrochemical behavior might be due to the active sites, reaction kinetics and surface area of the active regenerated graphite. In another words, expanding the interlayer spacing of graphite leads to enrich the higher cation storage resulting in the efficient electrochemical performance [1, 37]. Also, enhancement of interlayer spacing causes the reduction in the graphite particle size at the same time increases the pore size of the same, thereby overwhelmed electrical performance is attained [1]. The pore size, particle size and surface area significantly alter the storage behavior of the active sample.

The waste foam incorporated binder samples reveals the poor electrochemical performance when compared to PVdF used as binder. This might be due to the lesser amount of generated current via lower transfer of electrons that reduces the electronic conductivity, which in turn reduces the interfacial conductivity also. Thereby, nearly half of the capacitance value has been dropped. This may be sort-out by further modifications in the content percentage of foam, which is beyond the scope of the current work. In similar vein, Machado et al [19] has reported the preparation of magnetic activated carbon material by a two-step conventional method with use of wasted polystyrene foam as a precursor compound. This is the foremost study to prepare magnetic carbon compounds from the plastic sponge. They have evaluated its adsorbent characteristics with varying the composition and types of adsorbates and their results are discussed. On the other hand, energy storage properties also studied and demonstrated the highest specific capacitance of 334.4 F g$^{-1}$ towards redox behavior based SC applications.

Figure 9 represents the GCD plots of as-prepared graphite samples at several current densities. All the GCD curves are found to exhibit a similar nature, and almost the same for all the current density values, which indicates the good reversible nature of the graphite samples. In comparison with the GCD plots of all graphite samples, the PVdF and RG samples show a much higher discharging time which indicates better non-Faradaic charge storage characteristics. This result is probably ascribed to the lower transfer resistance via good inter-contact among graphite flakes and binder thus supports the ionic migration. The significant improvement in performance is due to the existence of efficient electron withdrawing group as well as higher dielectric constant of the binder. This helps to enrich the transportation of cations and produces the lots of mobile ions [38, 39]. In contrast, RG with polystyrene foam reveals poor performance, which may be due to progressive lose of electrical contact, kinetics of ion transport and thereby increasing the resistance and prevents the ion transportation as a result lesser discharging time. A similar observation is made for the commercial graphite samples. More specifically, the waste polystyrene foam does not contribute sufficient conductivity as well as contact to employ as a binder material without losing the electrical storage characteristics of RG and CG. This may be resolved via modification and optimization process of polystyrene content. Because, PVdF and polystyrene polymer network has the distinct functional groups on their
backbone thereby plays a prominent role in electrical contact among electrode material and current collectors. Based on the achieved results, reclamation of graphite from spent LIB is an alternate research and interesting direction as well. This may be applicable to the upcoming robust energy sectors.

3.5.2. Electrochemical evaluation of regenerated graphite in symmetric configuration

In order to investigate the potential viability of regenerated graphite in device operation, SSC has been fabricated with the geometry of RG| GPE| filter paper as a separator | RG. Figures 10(a) and (b) represents the CV curves for the assembled symmetric device with use of RG/PVdF and RG/Foam and cell potential of the SSC has been selected as the range between 0 to 1.4 V. This cell voltage is greater than the previously reported graphite SSC [40]. In particular, CV plot is observed to be a rectangular in nature within the range of cell voltage. In order to determine the reversibility of this cell potential, fabricated device has been studied for several sweep rates from 10 to 100 mV s$^{-1}$. From the multiple scan rates, performance of the CV pattern remains similar without any variation in the sweep areas, which signifies the reversibility of SC device. This result is a good indication for further progression of the research direction towards the regeneration of spent graphite compound.

The areal capacitance of fabricated SSC has been calculated with reported equation [35]. The predominant areal capacitance of 57 mF cm$^{-2}$ is obtained for PVdF used RG at 10 mV s$^{-1}$, whereas higher scan rate (100 mV s$^{-1}$) unveiled capacitance value of 34 mF cm$^{-2}$. The as-fabricated symmetric device represented good rate capability in terms of higher areal capacitance retention ratio, around 60% between lower and higher sweep rates. Besides, the polystyrene foam-RG device displays the areal capacitance of 38 mF cm$^{-2}$ at 10 mV s$^{-1}$ and 20 mF cm$^{-2}$ at 100 mV s$^{-1}$ with the retention of 53%. The deviation in value of areal capacitance with increasing scan rate of the device is attributed to short time contact between electrolyte ions and active graphite electrode thereby losing the surface charges resulting in the limited accessible area for the storage of charge [41].

The GCD curves of SSC is given in the figures 10(c) and (d) at several current densities. The assembled device exhibited almost symmetrical type and triangular curves with a smaller IR drop value for the whole range of current densities, which further confirms the supreme property of symmetric EDLC and excellent
reversibility of the RG electrodes. More importantly, the obtained GCD curves signify the linear variation of voltage with respect to time during charging and discharging process. Thus, it has been confirmed that the fabricated device holds good electrical performance. The estimated areal capacitance of PVdF binder used SSC is found to be 131, 120, 115, 111, 108, 107 and 90 mF cm$^{-2}$ for 2, 3, 5, 6, 7, 8 and 9 mA cm$^{-2}$ respectively. Whereas foam used RG based SSC demonstrated the values of 37, 36, 35, 34, 33, 32, and 31 mF cm$^{-2}$ for the similar current densities of PVdF used SSC. The durability and stability of both the devices has been tested for multiple charge/discharge cycles, and its cycling strength is shown in the figures 11(a) and (b). It is worth mentioning that the assembled SSC retains the specific capacitance of 67 mF cm$^{-2}$ with a greater retention ratio of 62.2% compared to foam assisted SSC. However, both the SSC maintains stable coulombic efficiency, which indicates the good reversibility of the device.
Figure 12. Nyquist plots of fabricated supercapacitor (a) RG with PVdF (b) RG with Foam.

The power (mW cm$^{-2}$) and energy density (mWh cm$^{-2}$) of SSC has been computed from literature [35]. As found, higher energy density of 8.9 mWh cm$^{-2}$ with power density of 128.88 mW cm$^{-2}$ is achieved for PVdF/RG SSC whilst foam/RG device reveals lesser value around 2.5 mWh cm$^{-2}$. Furthermore, lower areal energy of 4.5 mWh cm$^{-2}$ holds greater power density and the value is found to be 516 mW cm$^{-2}$, which indicates the excellent charge storage capabilities of the assembled SSC as an alternate energy storage device. Even after 1000 cycles, the as-prepared PVdF/RG assisted SSC regains its areal power of 449 mW cm$^{-2}$ with energy density of 4.5 mWh cm$^{-2}$.

The Nyquist plot for the assembled RG device is portrayed in figures 12(a) and (b) and it contains the higher frequency semicircle and diagonal spike portion at lower frequency regime. The semicircle is an indication for the parallel combination of resistance and capacitance thereby determines charge transfer resistance ($R_{ct}$) across the boundary of electrode/electrolyte. The slanted line is ascribed to the impact of ion blocking phenomena over the electrode/electrolyte interface. The inset figure shows the equivalent circuit model and is fitted by Z-view software. Before and after cycling, the diameter of the semicircle portion seems to be increased, which means an increment in the $R_{ct}$ value. The estimated $R_{ct}$ values are found to be 0.57 Ω and 4.2 Ω for before and after cycles respectively. In the case of RG with foam, the value of $R_{ct}$ is 2.35 Ω and 5.14 Ω. EIS results also confirms that the foam used RG sample shows the higher interfacial resistance and needs modification in the aspect of energy storage properties. The reason behind the increment in $R_{ct}$ value is the lack of contact between electrode and electrolyte interfaces and irreversible insertion of cations in active graphite electrode by escalating the cycles thereby reducing the active sites. From the several physicochemical and electrochemical analyses, the regeneration of graphite from spent LIB is opening door for future need towards the sustainability and waste to wealth technology.

4. Conclusion

The graphite restoration is successfully achieved from spent LIBs without any heavy metals beings present using a simple acetic acid curing procedure. The physicochemical and electrochemical properties of as-regenerated graphite and commercial graphite is compared and discussed. As an outcome, restored graphite exhibits superior electrical performance to that of commercial graphite. A Rietveld XRD result reveals that the reclaimed graphite maintained its original crystal structure without any impurities. Interestingly, impact of binder on the electrochemical performance of graphite samples has been studied and compared. The maximum areal capacitance of 285 mF cm$^{-2}$ is attained for the regenerated graphite with PVdF as a binder whereas polystyrene foam used RG shows the capacitance value of 164 mF cm$^{-2}$.

Assembled symmetric SC exhibits excellent stability over the 1000 cycles, which proves the durability of the same. Using the current process, regeneration of graphite turned at to be a cost-effective and sustainable approach for the anode utilization from spent lithium storage devices. These findings indicate as-restored graphite can be employed as an anode material for novel energy storage devices. A word of caution on useful reclamation of graphite from spent LIBs is the prior information on the number of cycles LIBs has gone through and LIB chemistry to obtain uniform product quality.
Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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Author contributions

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Conflict of interest

The authors declare that they have no conflict of interest.

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