Plasma jet printing induced high-capacity graphite anodes for sustainable recycling of lithium-ion batteries

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Abstract

Graphite is an integral part of lithium-ion batteries (LIBs). However, due to limited resources and high production cost of the highly purified (battery grade) graphite are becoming a challenge to meet the ever-increasing demands for energy storage devices. One viable approach is to recycle the spent graphite anodes from end-of-life LIBs. Importantly, recycling of spent lithium-ion batteries (LIBs) is of utmost importance to address the global challenge of electronic waste management. Herein, we present an environment friendly technique of graphite recycling from the spent LIB by water leaching, followed by atmospheric plasma jet printing. The major advantage of this method is that it does not require any binders or conductive diluents. Plasma printed recycled graphite showed significantly enhanced specific capacity of 402 mAh g\(^{-1}\) at 500 mA g\(^{-1}\) at the end of the 1000\(^{th}\) charge-discharge cycles, in comparison to water-washed recycled graphite (112 mAh g\(^{-1}\)) and an 23.35 times faster diffusivity of Li\(^+\). A detailed experimental investigation revealed the plasma activation of the graphitic structure resulted in the improved reversible Li\(^+\) storage. This work provides a new perspective on the recycling strategy of graphite anodes using the in-situ plasma functionalization strategy, a significant step towards the sustainable future of LIBs.
1. Introduction

Carbonaceous materials are extensively studied as an anode material in lithium-ion batteries due to low redox potential, high specific capacity, and its earth abundance.[1,2] Graphite is the state-of-art anode material used in most commercialized LIBs due to its high conductivity of $10^3$ S cm$^{-1}$ and a theoretical capacity of 372 mAh g$^{-1}$ (a stoichiometry up to LiC$_6$) in the potential operating range of 50-200 mV vs. Li/Li$^+$. [3] The reversible intercalation/ deintercalation mechanism of Li$^+$ and high structural stability on the cycling process inspire the breakthrough of graphite as an anode in LIBs. Other than graphite, carbon nanotubes (CNTs) [4], hard carbon[5], soft carbon,[6] and graphene are the other promising anode materials for LIBs.[7–9] Graphene is a 2D nanostructured $sp^2$ carbon material, which can be formed from the exfoliation of bulk graphite.[10,11] Graphene can accommodate a high amount of lithium on both sides, edges, and covalent sites resulting in a high capacity of 744 and 1448 mAh g$^{-1}$ based on Li$^+$ intercalation property such as Li$_2$C$_6$, or Li$_4$C$_6$, respectively.[7–9,12–14] However, graphene has high irreversible capacity loss and limited cycle life. Thus, graphite is still the choice of LIB anode for various commercial applications. Further, the demand for high-quality and 99.9 % purity commercial battery-grade flake graphite is gradually increasing 10-12% per year and limits its availability.[15]

Rechargeable lithium-ion batteries (LIBs) are widely used in portable electronic devices, power tools, medical devices, hybrid/electric vehicles (HEV and EVs). This is due to their lightweight, high energy-density (150-250 Wh/kg), high operating voltage (3.7 V), low self-discharge rate (1-5 % per month), increased cycling stability (>1000 cycles). [16–18] This accelerated production has translate into enormous amount of battery waste with several adverse environmental impacts. Therefore, recycling and reuse of cell components is of utmost importance to address the economic and environmental challenges of LIBs waste. Over the
years, the main aim for the recycling industries have been to recover valuable metals (e.g., Al, Ni, Co, Mn, Li, Cu, etc.). However, less attention been paid to the recycling of anode for low value-added graphite and rigorous separation steps. Umicore, Inmetco, and some other companies follow the pyro-metallurgical process where graphite is burned in the smelter furnace at a high temperature above 1000°C to supply the high processing energy to recover metals and alloys.[19–21] However, the hydrometallurgical process can recover the graphite of low purity based on solvent extraction and filtration techniques.[22,23] Some pre-treatment studies are reported on the direct physical recycling process, including dismantling, crushing, sieving, and other mechanical steps to recover graphite of high quality but are limited to lab-scale.[24] Previously, research efforts were directed on recycling graphite anode from spent LIBs for fresh LIBs and preparation of high-performance graphene in recent years. Reported graphite recovery techniques are based on leaching in n-methyl-2-pyrrolidone (NMP), HCl-H$_2$O$_2$ mixture, H$_2$SO$_4$-H$_2$O$_2$ mixture, or aqueous acid mixture followed by further modification (e.g., chemical treatment, calcination) to restore the graphite in an electrochemically active state.[25–33] The solid electrolyte interface (SEI) formed on graphite surface retains integrated graphitic structure in cycled graphite with little change of surface composition. The interlayer spacing may increase up to 10.3% on co-intercalation of Li$^+$ and electrolyte solvent molecules.[34] A comparison table of graphite recovery, post-modification techniques, their obtained specific capacity, and capacity retention with respect to cycle number are presented in the Table 1.
<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Separation from current collector</th>
<th>Post modification</th>
<th>Initial Stable discharge capacity in approx. (mAh g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Current density (mA g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Cycle number</th>
<th>Capacity retention wrt. 1&lt;sup&gt;st&lt;/sup&gt; cycle (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>Electrolysis [26]</td>
<td>-</td>
<td>(i) 427.81 (ii) 315</td>
<td>(i) 37.2 (ii) 186</td>
<td>(i) 50</td>
<td>(ii) 84</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>(ii) 85</td>
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<td>2</td>
<td>Heating under argon atm. at 400°C, 1hr [27]</td>
<td>HCl-H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>(i) 591 (ii) 172.6</td>
<td>(i) 37.2 (ii) 372</td>
<td>(i) 1</td>
<td>(ii) 96.5</td>
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<td>3</td>
<td>Alcohol leaching [29]</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt; then heating 750°C, 8hr, N&lt;sub&gt;2&lt;/sub&gt; atm.</td>
<td>360</td>
<td>186</td>
<td>200</td>
<td>85.5</td>
</tr>
<tr>
<td>4</td>
<td>Mechanical separation [30]</td>
<td>DI-water washing</td>
<td>345</td>
<td>74.4</td>
<td>100</td>
<td>&gt;99</td>
</tr>
<tr>
<td>5</td>
<td>Manual dismantling [31]</td>
<td>Smelting in N&lt;sub&gt;2&lt;/sub&gt; atm.- ultrasonic vibration, sieving</td>
<td>361.52</td>
<td>372</td>
<td>100</td>
<td>99.8</td>
</tr>
<tr>
<td>6</td>
<td>Crushing – sieving– H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;-H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt; (separation of anode from cathode-anode mixture) [25]</td>
<td>sintering with NaOH powder and then DI-water washing</td>
<td>350</td>
<td>74.4</td>
<td>100</td>
<td>84.63</td>
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<td>7</td>
<td>Spent graphite [32]</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt; curing - DI-water washing-and calcination at 1500°C, 2hr, N&lt;sub&gt;2&lt;/sub&gt; atm.</td>
<td>349</td>
<td>37.2</td>
<td>50</td>
<td>98.8</td>
</tr>
<tr>
<td>8</td>
<td>Manual dismantling [33]</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;-H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt; then heated 300-600°C in air - DI-water washing and drying</td>
<td>350</td>
<td>37.2</td>
<td>50</td>
<td>91</td>
</tr>
<tr>
<td>9</td>
<td>Manual dismantling - DI-water leaching (This work)</td>
<td>Plasma jet printing</td>
<td>490</td>
<td>500</td>
<td>1000</td>
<td>82</td>
</tr>
</tbody>
</table>

Electronic copy available at: https://ssrn.com/abstract=4109795
Previously, it has been demonstrated that an atmospheric pressure plasma jet (APPJ) could be used to print nano-colloid inks and in-situ tune the surface chemistry and electronic properties of the printed material.[35] Herein, we propose an eco-friendly leaching method of spent graphite anode by facile water treatment, followed by in-situ plasma printing of the recycled graphite on to the copper foil current collector and used as an anode material for LIBs. The key advantage of this method is that plasma printed graphite architecture contains no additional additives such as conductive diluents and binder unlike conventional methods, thus resulting in greater utilization of total active material. Furthermore, the in-situ surface modified oxidized functionalities in the graphite matrix incorporate higher specific capacity than conventional graphite anode. The irreversible capacity loss in the charge-discharge cycling process is partially reduced as graphite lattice can withstand the aggregation of graphene sheets and provide structural stability, enhancing Li⁺ kinetics.[36] Our electrochemical studies indicate that the recycled plasma printed graphite thin film electrode exhibits good C-rate performance and cycling stability with an enhanced specific capacity of 490 mAh g⁻¹ and 82% capacity retention over 1000 cycles at 500 mA g⁻¹. This work presents a novel approach to recover the anode from spent lithium batteries and subsequent in-situ oxidation and atmospheric pressure plasma jet printing on to copper, which not only reduce the cost and efficiency of electrode but also facilitates environmental protection and circular economy.

**Table 1:** A comparison table of anode separation method from spent LIBs, post-modification techniques of recovered graphite, achievable specific capacity and capacity retention with respect to C-rate and cycle life.
2. Experimental

2.1. Recovery of graphite from spent Li-ion battery

18650 type cylindrical cells were obtained from a spent laptop battery pack supplied by Nile Limited, Hyderabad, India. The cells were discharged below 2 V for safety issues and then dismantled manually. From the electrode assembly, the anode part was carefully taken out. Anode was separated from the copper foil current collector under vigorous stirring in distilled water at 1200 rpm for 30 minutes at room temperature. It was then filtered and dried overnight at 90°C. Water washing removes most of the residual lithium from the graphite surface by hydrogen evolution reaction and unwanted impurities of SEI, restoring electrochemically active graphite.

2.2. Plasma printing of recovered graphite

The graphite suspension was prepared by dispersing 0.5 g of graphite powder in 20 ml of 2 methoxy ethanol. The dispersion was then ultra-sonicated using a high-power ultrasonic probe for 5 minutes to get a stable colloidal suspension used as the graphitic ink. This ink was then used to print on to copper foils of 2.5 cm x 2.5 cm dimension. Before printing, the copper foils were etched in 1 M HCl washed with isopropyl alcohol to remove surface oxides, impurities, and 10 ml of ink was used for deposition on to individual foils. During the printing, the foils were placed on a hot plate at 170 °C, and the plasma jet trigged with power 120 watts using He as carrier gas was made to raster over the foil to get a uniform and compact film. Details about the plasma printing setup are presented in the supplementary section S1.
2.3 Structural and morphological characterization

The XRD measurements of the water-washed and plasma-printed recycled graphite films were measured using an X’Pert Pro diffractometer (The Netherlands) (reflection θ- θ geometry, Cu Kα, λ=1.54 Å radiation, receiving slit of 0.2 mm, scintillation counter, 30 mA, 40 kV). The diffraction data were collected between the 2θ value 5° and 70° with the scan rate of 0.016 deg s⁻¹. The surface morphologies of the as-synthesized material were further measured by scanning electron microscopy (ZEISS FE-SEM, Germany). X-ray photo electron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy were carried out at the near-ambient-pressure XPS end station of beamline B07 at Diamond Light Source[37] to understand the changes in surface chemistry of carbon and electronic properties with and without plasma treatment. The beamline provided linearly polarized light with a bending magnet as source. The beam hit the surface under an angle of 24° with an angle of 40° between the polarization vector and the surface normal. All spectra were acquired at room temperature (22°C) and under high vacuum with a base pressure of (1–5) ×10⁻⁸ mbar. The photoelectron spectra were recorded at near-normal emission (5° off). For the surface sensitive C1s scans, a photon energy of approximately 490 eV was used with a pass energy of 40 eV, monochromator exit slits gap at 50 µm, and a grating of 400 lines/mm. For the C1s scans at higher energy (more bulk sensitive) the photon energy was set to 1408 eV using a grating of 800 lines/mm. The binding energy scales are calibrated by setting the Au4f⁷/₂ peak to 84.00 eV. The NEXAFS spectra were measured via the total electron yield, measured via the cone of the differentially pumped analyzer. For these measurements, a grating with 400 lines/mm was used and the exit slit gap were set at 25 µm. The photoelectron spectra were analyzed using Casa XPS software. Core lines were fitted with a 50% mixture of Gaussian and Lorentzian line shape functions after a Shirley background subtraction to maintain the residue <1. Raman spectra were measured using a Horiba Jobin-Yvon LabRAM HR evolution spectrometer using an Ar⁺ laser with a
514.5-nm line as the excitation source. The laser power was kept at \(~0.5\) mW for these measurements to minimize any effect of heating.

2.4 Cell assembly and electrochemical characterization

The electrochemical performances were conducted using CR2032 type coin cells. The plasma printed recycled graphite thin film electrode was punched into a 1cm\(^2\) area electrode and used as it is. The active material loading of the plasma printed recycled graphite electrode was \(~0.5\) mg cm\(^{-2}\). Conventional electrodes were prepared from a slurry of 85% of water-washed recycled graphite as active material, 5% C-black additive, and 10% sodium carboxymethyl cellulose binder distilled water. The slurry was coated onto copper foil using a doctor blade and dried under vacuum at 80 \(^\circ\)C overnight. The electrodes were calendered and punched into a circular disc of 1 cm\(^2\) area. The cells were fabricated inside an argon-filled glove box (mBraun, Germany) with O\(_2\) and H\(_2\)O levels less than 0.1 ppm using lithium metal foil as reference and counter electrode. The electrolyte used was standard LiPF\(_6\) in 1:1 ethylene carbonate-diethyl carbonate. The electrochemical measurements such as cyclic voltammetry, galvanostatic charge-discharge, cycling performance, C-rate at different current densities were tested between the potential range of 0.01-1.5V using the battery test unit model 1470E coupled with an FRA model 1455A from Solartron Analytical (Oak Ridge, TN, USA) instruments. The cyclic voltammetry was recorded at a scan rate of 0.05 mV s\(^{-1}\). Electrochemical impedance spectra were carried out between 100 kHz to 10 mHz with the voltage perturbation at 5 mV in an open-circuit condition before cycling, 1\(^{st}\) and 1000 cycles.
3. Results and discussions

3.1 Structural and morphological characterizations

Figure 1. SEM images of (a), (b) water-washed graphite; and (c), (d) plasma printed recycled graphite of different magnifications.

Morphology of water-washed and plasma printed recycled graphite particles are shown in SEM images (figure 1). The water washed graphite is mainly of inhomogeneous morphology, with varying size distribution (15-20 µm), as seen from Figure 1a. It is known that continuous cycling of the graphite anode results in the exfoliation of the graphite flakes.[34] At higher magnification (figure 1b), the lamellar structure of the graphite particles is visible. On the other hand, the plasma-printed graphite (figure 1 c-d) has undergone a significant change in surface morphology and is having primarily spherical particles and flakes (figure 1d). This indicates the effective exfoliation of the graphite particles during the plasma printing process. Moreover, the plasma-printed graphite has a noticeably smooth and flat surface. Previous studies have shown that a smooth and flat surface of graphite facilitates the infiltration of electrolytes between the graphite particles and may improve the electrochemical performance of the anode.[32,38]
Figure 2. (a) Raman spectra of plasma printed and water-washed recycled graphite, (b) deconvoluted D and G Raman bands for plasma printed recycled graphite; (c) XRD data of water-washed and plasma printed recycled graphite, (d) zoomed image of (002) peak in the XRD pattern

The structural integrity of the plasma printed graphite films characterized using Raman spectroscopy in figure 2a-b shows the vibrational modes related to the graphitic structures have distinct features in the Raman spectra. The spectra shown in Figure 2a consist of two peaks, assigned to the D band at 1353 cm\(^{-1}\) and to the G band at 1586 cm\(^{-1}\), which are typical of a \(sp^2\) structure. An additional second-order peak at 2740 cm\(^{-1}\) represents the 2D band.\[35\] For water-washed graphite, the G and 2D bands dominate the spectra. The ratio between the intensity of these G and 2D bands evolves with the number of graphene layers. As the number of layers increases, the intensity of the G band increases significantly, while that of the 2D band decreases. The low energy D band requires defects in the graphitic structure for its activation.\[39\] However, the sharp G band show long-range graphitic order is still preserved. The peak-fitted D and G Raman bands of the plasma-printed graphite film in Figure 2b show the D band fitted with a single Lorentzian function while the G band consists of three features. In addition to the
peaks centered at 1353 cm$^{-1}$ and 1586 cm$^{-1}$, which corresponds to the conventional D and G bands, two other peaks at $\sim$1535 cm$^{-1}$ (D**) and $\sim$1615 cm$^{-1}$ (D') are observed.[40] The D' band corresponds to the defects induced intra-valley transitions. On the other hand, the D** peak due to reduced crystallite size or due to C-H vibrations of hydrogenated $sp^2$ carbon atoms.[41] From the Raman spectra, plasma-printed graphite films show abundant defects and smaller crystallite sizes. The ratio between the intensities of D-band ($I_D$) and G-band ($I_G$) signifies the degree of graphitization of plasma printed and water washed recycled graphite. Compared to water-washed graphite flakes with $I_D/I_G$ of 0.15, the printed graphite film shows an $I_D/I_G$ of 0.79 with a broad and intense D peak, indicating the defect sites from the surface functionalities. As seen from the XRD pattern (figure 2c), the bulk graphitic structure is preserved after plasma-jet printing of the extracted anodes. Both the graphitic samples show a strong diffraction peak at about 26°, characteristic of the (002) plane of graphite. However, the printed graphite peak exhibits a slight shift toward a lower 2θ value, as shown in figure 2d. This shift could be due to the increase in interlayer distance of the graphitic planes. The interplanner distance ($d_{002}$) is calculated using Bragg’s law i.e.$d_{002} = \frac{\lambda}{2 \sin \theta}$; where $\lambda$ is the Cu-kα radiation wavelength of 1.5406 Å. The value of $d_{002}$ is increased to 3.3408 Å for plasma printed recycled graphite compare to water washed graphite of 3.336 Å which signifies a slight exfoliation with respect to the extracted graphite. This shift can also be attributed to an increase in structural defects. The peak around 19° could be from the lithium based transition metal oxide cathodes (metals could be Ni, Mn, Co). There is a noticeable increase in the relative intensity of the impurity peak at 19°. This might be due to the aerosolization process, where lighter particles are carried through to the substrate.
Figure 3. XPS spectra of (a) water-washed recycled graphite and (b) plasma printed graphite. (c) C 1s spectra of plasma printed graphite with different photon energies (d) near-edge X-ray absorption fine structure (NEXAFS) spectroscopy of water-washed recycled graphite and plasma printed graphite.

X-ray photoelectron spectroscopy (XPS) along with near-edge X-ray absorption fine structure (NEXAFS) spectroscopy were used to understand the element specific surface chemical states of the plasma-printed films. In XPS, the spectral feature is strongly dependent on the bonding and composition of carbon in these graphitic films. In contrast to XPS, NEXAFS spectra are governed by dipole-allowed transitions making it more discreet towards the chemical structure being mapped and gives information on unoccupied density of states.[35] Figure 3 shows the C1s XPS and C K-edge NEXAFS spectra of water-washed recycled graphite and plasma-printed graphite. The carbon spectra for water-washed recycled graphite has a dominant peak at 284.4± 0.1 eV, corresponding to the $sp^2$ carbon of the graphite structure.[42] The sharp profile (FWHM = 0.66 eV) with asymmetric tail is typical for graphite, due to its metallic nature. Notably, the C1s spectra of graphite have a contribution from carbon in multiple distinct chemical environments between 285 and 292 eV. The component at 285.5 ± 0.1 eV is attributed
to hydrocarbons (C-H), while the structure at 287.2 ± 0.1 eV, is attributed to carbon atoms bonded to a single oxygen atom via a single bond (C-O), and the fourth peak at 289.3 eV, is assigned to carbon atoms double-bonded to an oxygen atom (C=O). C-O contributions could be from the epoxide and hydroxyl moieties,[43] while the C=O could originate from carboxylic acid, quinoidal, ketone, and lactone groups.[44] The higher energy component at 291.4 ± 0.1 eV corresponding to the plasmon loss feature found in ordered graphitic structure. Previous reports have attributed the peak at 287 ± 0.1 eV to lithium alkyl carbonates (R–CH₂–OCO₂Li), the main components of the SEI formed on graphite electrodes.[45] Being a highly surface-sensitive technique, XPS indicates that the extracted graphite is highly perturbed with C-O/C=O and C-H species either due to repeated cycling or from the extraction water leaching process.

Figure 3b shows the C₁s core level photoelectron spectra of the plasma-printed graphite electrode. For the printed graphite, the spectrum is more symmetric with broader components. The main (C-C) peak is shifted to higher binding energy 284.8 ± 0.1 eV and is much broader with respect to water-washed graphite (FWHM= 1.20 eV). This is typical for defects in the aromatic ring, as sp³ carbon has higher binding energy with respect to sp²-hybridized carbon. The relative concentration of hydrocarbons and oxygen moieties has increased for plasma-printed graphite. In our case surface oxidation caused by the interaction with plasma or aerosolization could be a plausible suggestion. These two spectra were acquired with a photon energy of 490 eV so as to probe highly surface sensitive components and its contribution to the surface chemistry of the films. To probe deeper (bulk contribution) into the surface, C₁s spectrum for the printed film was acquired with a higher photon energy of 1408 eV (figure 3c). The striking feature is, the components above 286 ± 0.1 eV diminishes at the higher photon energy showing a lower degree of oxidation in the bulk while rest of the line shape remains the same. Additionally, NEXAFS at the C-K edge in TEY mode was used to complement the XPS. Water-washed recycled graphite has a well-defined π-resonance at 285.5 ± 0.1 eV and sharp resonance at 291.7 ± 0.1 eV, typical of graphite. The peak at 285.5± 0.1 eV corresponds to
1s–π* transitions of the C=C structure of the carbon lattice, and the 291.7± 0.1 eV peak corresponds to the sharp C 1s core exciton and marks the transition to σ* states.[46] These two resonances are often referred to as a measure of the structural integrity and long-range order of the carbon structure. Though the printed graphite film has a strong π* resonance at 285.5 ± 0.1 eV resembling the predominant sp² nature, the absence of long-range order is obvious from the absence of the exciton feature at 291.7 ± 0.1 eV. This is often the case when graphite is oxidized. In addition to these core resonances, three additional features are observed in the printed graphite, marked as a, b, and c at 287.6 eV, 288.6 eV, and 290.7 eV corresponding to π* transitions of C–H, C=O, and σ* transitions of C-O, respectively.[44] Surface oxidation of graphite has been reported to have a profound influence on its properties as electrode material. The controlled presence of oxygen functional groups on the graphite surface increases the capacity significantly.[47] It has also been reported that C–H bonds facilitate fast lithium transport and reversible surface binding of graphene nanofoam electrodes in lithium-ion batteries.[48] A similar high capacity and stability is observed in the plasma-printed graphite electrodes due to the synergistic effects of surface oxygen moieties, C-H bonds, and sp² structure.

3.2 Electrochemical performance
Figure 4: (a) Cyclic voltammetry of plasma-printed recycled graphite at a scan rate of 0.05 mV s\(^{-1}\), (b) galvanostatic charge-discharge voltage profiles of water-washed and plasma printed recycled graphite at 30 mA g\(^{-1}\) in the potential range of 0.01-1.5 V.

To examine the Li-ion storage property of plasma printed recycled graphite electrode, cyclic voltammetry (CV) was performed in the voltage window between 0.01 and 1.5 V at a scan rate of 0.05 mV s\(^{-1}\). Figure 4a shows the CV curve during the lithiation and delithiation process at the 1\(^{st}\), 5\(^{th}\), and 1000\(^{th}\) cycles. A broad reduction peak ~ 0.8 V in the 1\(^{st}\) cycle appears due to electrolyte reduction on the graphite surface and formation of solid electrolyte interface (SEI). Two redox peaks below 100 mV confirm the stepwise formation of LiC\(_{12}\) and LiC\(_{6}\) phases on Li\(^+\) intercalation to graphite layers.[49] CV curves during 1000 cycles indicate good electrochemical stability of the plasma printed recycled graphite electrode. The CV curves for the water-washed recycled graphite show similar redox behavior and is presented in supplementary figure S2. The galvanostatic charge-discharge profile of plasma printed graphite and water-washed recycled graphite electrodes shown in figure 4b and supplementary figure S3 at a low current density of 30 mA g\(^{-1}\) indicates plasma printed recycled graphite electrode delivers an initial lithiation capacity of 786 mAh g\(^{-1}\) and a delithiation capacity of 698 mAh g\(^{-1}\), respectively with an irreversible capacity loss of 11 % in the 1\(^{st}\) cycle and 6.5% in the 2\(^{nd}\) cycle. The peaks in the CV curve (figure 4a) during the lithiation process, which shows SEI,
LiC\textsubscript{12}, LiC\textsubscript{6} formation, are in good agreement with the observed potential plateau in the discharge profile. However, water-washed recycled graphite exhibits a comparatively lower lithiation capacity of 446 mAh g\textsuperscript{-1} and delithiation capacity at 330 mAh g\textsuperscript{-1} in the 1\textsuperscript{st} cycle, which corresponds to irreversible capacity losses are 26 % during 1\textsuperscript{st} cycle.

![FIGURE 5: Charge-discharge profile of (a) plasma printed recycled graphite electrode and (b) water-washed recycled graphite electrode; and (c) capacity vs. cycle number plot at 500 mA g\textsuperscript{-1} in the potential range of 0.01-1.5 V.](image)

Plasma-printed recycled graphite electrode was exposed to high rate cycling at 500 mA g\textsuperscript{-1} current density for 1000 cycles after two formation cycles at 30 mA g\textsuperscript{-1} and the electrochemical performance was compared with the cycling studies of water-washed recycled graphite electrode under similar conditions. The galvanostatic charge-discharge profile of both the electrodes for the 5\textsuperscript{th}, 500\textsuperscript{th}, and 1000\textsuperscript{th} cycle at 500 mA g\textsuperscript{-1} in the voltage range of 0.01-1.5 V are shown in figure 5a-b. Plasma-printed recycled graphite electrode exhibits good cycling
stability over 1000 cycles at 500 mA g\(^{-1}\) current density (figure 5a and 5c). It delivers stable initial lithiation capacity of 490 mAh g\(^{-1}\) and delithiation capacity of 486 mAh g\(^{-1}\) at 500 mA g\(^{-1}\) with 99% coulombic efficiency. At the end of the 1000\(^{th}\) cycle, the plasma-printed recycled graphite electrode shows 82% capacity retention with lithiation capacity of 402 mAh g\(^{-1}\) and delithiation capacity of 400 mAh g\(^{-1}\) with >99% coulombic efficiency. Whereas, water-washed recycled graphite electrode delivers initial discharge capacity at 195 mAh g\(^{-1}\) with 57% capacity retention at the end of the 1000 cycles (figure 5b and 5c).

The presence of heteroatom functionalities in the defect sites, as confirmed from XPS (figure 3a-c) and Raman studies (figure 2a-b), incorporate the extra achievable capacity in plasma printed recycled graphite compare to water-washed recycled graphite electrode. Electron donating heteroatoms such as oxygen-containing functional groups increases the electron density in graphene sheets that favors the higher possibilities of Li bonding. Moreover, H-functionalities such as C-H, hydroxyl, carboxyl groups in the edge sites improve the lithium storage capacity by surface adsorption and open up more space for Li\(^+\) transportation and intercalation into the graphite layers.[48] A schematic sketch explaining different phases of Li\(^+\) storage mechanism into the plasma printed recycled graphite is shown in figure 6.[8,50] The increase in the interlayer distance between the graphene sheets as shown in XRD (figure 2d) can accommodate lithium in both the faces of the graphene layers. The reversible Li-ion storage phenomena in plasma printed recycled graphite electrode results in >99% coulombic efficiencies during the cycling process (figure 5d). The sloping curve in voltage vs. capacity plot above 0.2 V vs. Li/Li\(^+\) in plasma printed recycled graphite signifies the adsorption-chemisorption of Li\(^+\) in the edges and Li\(^+\) bonding with surface heteroatoms of graphite moieties. The plateau profile below 0.2 V (figure 4b) indicates the stepwise intercalation of Li-ions into the graphite layers. The hysteresis curve (supplementary figure S3) of specific capacity vs. voltage is compared between plasma printed and water-washed recycled graphite to observe this hypothesis. The voltage profile below 0.2 V is similar in both cases. However, in the
voltage range between 1.5 and 0.2 V, plasma printed recycled graphite shows 290 mAh g\(^{-1}\) capacity, which is much higher than water-washed recycled graphite (e.g., 49 mAh g\(^{-1}\)) due to the surface-induced lithium adsorption (supplementary table ST2). Li\(^+\) accommodate on both sides and edges, introduces additional specific capacity. The synergistic effect of oxidized graphite, and graphitic lattice of plasma printed recycled graphite provide high specific capacity with stable capacity retention over 1000 cycles.

C-rate performance and voltage profile of plasma printed recycled graphite electrode in both low and high current densities are shown in figures 7a and 7b. Average discharge capacities of 630 mAh g\(^{-1}\) at 100 mA g\(^{-1}\), 525 mAh g\(^{-1}\) at 500 mA g\(^{-1}\), 486 mAh g\(^{-1}\) at 1000 mA g\(^{-1}\), 388 mAh g\(^{-1}\) at 2000 mA g\(^{-1}\), 195 mAh g\(^{-1}\) at 5000 mA g\(^{-1}\), 105 mAh g\(^{-1}\) at 10000 mA g\(^{-1}\) have been achieved for plasma printed electrode, and when it returns to 100 mA g\(^{-1}\), the electrodes deliver 565 mAh g\(^{-1}\). In contrast, water-washed recycled graphite electrode shows negligible capacity at high current densities. This signifies good capacity retention of plasma printed recycled graphite electrodes both at high and low discharge rates with high-capacity retention.

![Figure 6. Pictorial representation of different phases of Li-ion storage phenomena into the plasma-printed graphite electrode.](https://ssrn.com/abstract=4109795)
Figure 7: (a) C-rate performance of plasma printed and water-washed recycled graphite electrodes and (b) charge-discharge profile of plasma printed recycled graphite electrode at different current densities in the potential range of 0.01-1.5V.

Figure 8: (a) Nyquist plot of plasma printed recycled graphite electrode (inset: zoomed image of the high-frequency part), and (b) The corresponding relationship between $Z'$ and $\omega^{-1/2}$ in the low-frequency region; (c) Nyquist plot of water-washed recycled graphite electrode (inset: zoomed image of the high-frequency part), and (d) The corresponding relationship between $Z'$ and $\omega^{-1/2}$ in the low-frequency region, after 1st and 1000 cycle.
Electrochemical impedance spectroscopy (EIS) was performed to further study the electrode kinetics. The significant specific capacities at high current densities are obtained due to fast faradic surface reactions inducing high Li storage capability. Nyquist plot ($Z' \text{ vs. } Z''$) of plasma printed recycled graphite, and water-washed recycled graphite electrodes were obtained at 1st cycle and 1000th cycle as shown in figure 8. The plot consists of a semi-circle and a linear tail at high frequency and low frequency, respectively, assigned to charge transfer resistance ($R_{CT}$) and Li$^+$ diffusion to the bulk of the electrode. The $R_{CT}$ of plasma printed recycled graphite electrode increases a little from 1st cycle (50 $\Omega$cm$^2$) to 1000th cycle (63 $\Omega$cm$^2$), indicating an excellent Li$^+$ transport into the matrix during prolonged cycling. Even though the variation of $R_{CT}$ values during cycling in water-washed recycled graphite is not increased significantly, the variation of the low-frequency linear tail is significant. The Warburg element at the low-frequency region is analyzed to understand Li-ion diffusivity within these electrode materials. The Li-ion diffusivity ($D_{Li^+}$) within water-washed recycled graphite and plasma-treated graphite is investigated using the slope of the graph between $Z'$ and the reciprocal square root of the frequency ($\omega^{-1/2}$) in the Nyquist plot as shown in Fig. 8b and 8d. The slope ($\sigma$) of the graph shown in figure 8b and d ($Z' \text{ vs. } \omega^{-1/2}$) of both the electrodes after 1st and 1000th cycling, demonstrating a linear relationship. The $\sigma$ value obtained here could be correlated to compare the diffusion coefficient before and after cycling as mentioned below.

$$\frac{D_x}{D_y} = \frac{\sigma_y^2}{\sigma_x^2}$$  \hspace{1cm} (1)

Therefore, \[ D_{1000} = \left( \frac{\sigma_{1st}}{\sigma_{1000}} \right)^2 \ast D_{1st} \]  \hspace{1cm} (2)

The Li-ion diffusivity in the plasma printed graphite electrode is reduced by almost 0.0816 times after 1000 cycles compared to the 1st cycle. In contrast, the water-washed recycled graphite electrode demonstrates a 0.1244 times reduction in Li$^+$- diffusivity during a similar cycling protocol. Further, the Li-ion diffusion in plasma printed graphite is almost 35.6 times higher than water-washed recycled graphite electrode after 1st cycle. It is worth noting here,
even after 1000 cycles, the Li-ion diffusion is 23.35 times higher in plasma printed graphite in comparison to water-washed recycled graphite electrode. Thus, the higher Li-ion diffusivity in plasma printed recycled graphite in comparison to water-washed recycled graphite electrode suggest the better electrochemical performance of plasma printed graphite, especially at a higher current rate of 0.5-10 Ag⁻¹, wherein water-washed recycled graphite electrode delivers almost negligible capacity at this high current rate, as shown in figure 7a.

Overall, the electrochemical studies reveal that plasma printed recycled graphite electrode delivers approximately twice the capacity of the water-washed recycled graphite electrode. The enhanced electrochemical performance is attributed to the controlled regeneration of surface chemistry with oxidized graphite and graphitic moieties in the same matrix via the plasma printing technique. Further, the plasma printed recycled graphite electrode does not contain non-conducting binders and conductive additives in the electrode preparation. These electrode fabrication techniques result in high specific capacity, good cycling stability, superior rate capability, and excellent electrochemical performance in plasma printed recycled graphite.

4. Conclusions
We propose an ecofriendly and efficient water leaching approach to recover graphite anode material from spent LIBs. The electrode preparation methodology by plasma jet printing technique eliminates conductive diluents and binders. Further, this method regenerates the surface chemistry of water-washed recycled graphite with incorporation of heteroatom functionalities and perturbed defect sites that were confirmed by XPS and NEXAFS studies. Both plasma printed and water-washed recycled graphite electrodes show similar stepwise Li-ion intercalation property into the graphite layers. However, the oxidized graphite moieties and adsorption-chemisorption of Li⁺ to the edges and both sides of the graphite sheet leverage the additional high specific capacity in plasma printed recycled graphite electrode. It delivers an enhanced capacity of 490 mAh g⁻¹ at 500 mA g⁻¹, with 82 % capacity retention over 1000 cycles, whereas water-washed recycled graphite delivered an initial capacity of 195 mAh g⁻¹, showed
57 % (112 mAh g\(^{-1}\)) capacity retention under similar condition. The excellent C-rate performance and cyclability of plasma printed recycled graphite electrode are due to the synergistic effect of oxidized graphite moieties and graphitic matrix. Besides, the diffusion studies from EIS spectra reveals the 23.35 times faster diffusivity of Li\(^+\) in plasma printed recycled graphite electrode than water-washed recycled graphite electrode even after 1000 charge-discharge cycles. This work shows a new avenue for green and sustainable recycling of spent LIB anodes to be reused as high-performance anode material for lithium-ion batteries using plasma printing technology. Much work needs to be done to identify the nature of these defects and to understand better the plasma jet influence on the electrode characteristics. The efficient process described herein will establish a solid foundation for the subsequent plasma deposition/printing processes in the recycling of spent batteries.

**Author Contributions**

This work was carried out under mentorship of Dr. Surendra K. Martha and Dr. Satheesh Krishnamurthy. Ms. Madhushri Bhar carried out material recovery, electrochemical characterizations and formal analyses. Dr. Avishek Dey carried out electrode preparation by plasma printing, physical characterizations and analysis. Ms. Madhushri Bhar, Dr. Avishek Dey, Dr. Sourav Ghosh, Dr. Dr. Surendra K. Martha and Dr. Satheesh Krishnamurthy wrote the complete manuscript. Dr. Sourav Ghosh carried out diffusion studies and Dr. Matthijs A. van Spronsen acquired the XPS and NEXAFS data. Dr. Vimalnath Selvaraj performed the XRD characterization. Mr. Y. Kaliprasad supplied spent LIBs and industry collaborator to the project. Dr. Satheesh Krishnamurthy and Dr. Surendra K. Martha are the coordinator from the funding acquisition.

**Conflicts of interest**

There are no conflicts to declare.
Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Table of contents
Here, we demonstrate an eco-friendly method to recycle graphite from spent Lithium-ion batteries (LIBs). High-capacity anodes are prepared by plasma jet printing of extracted graphite without the use of conventional additives. This study paves the way towards sustainable recycling of spent LIB anodes to be reused as high-performance anode material for LIBs using plasma printing technology.