

Special
Collection

Graphene from Spent Lithium-Ion Batteries

Madhusoodhanan Lathika Divya^{+[a]}, Subramanian Natarajan^{+[a]} and Vanchiappan Aravindan^{*[a]}



The fascinating properties of graphene continue to offer new dimensions in scientific research, extending its exploration in a wide range of real-world applications. At the same time, serious bottlenecks like low quality, high cost, negative reaction conditions, agglomeration of nanosheets, and limited mass production for graphene must be resolved in favor of industrialization. Consequently, utilization of large amounts of waste graphite from spent lithium-ion batteries (LIBs) offers a great opportunity to produce graphene and its derivatives to

partake in waste management and circular economy. This work sketches the progress in the different recycling techniques for the graphite anode from spent LIBs and their reuse in different applications. We believe our perspective can facilitate researchers/industries in the better reuse of graphite as valuable sources for the preparation of graphene in a high production capacity by breaking down the existing obstacles in the recycling process as well as helping to handle the upcoming massive volume of spent LIBs.

1. Introduction

Graphene, the world's first 2D material and the wonder material of the 21st century, has grabbed extensive research interest in the last twenty years due to its inherent unique properties, making it apt for a wide range of applications.^[1,2] It is just one atomic layer of graphite and is a single layer of sp^2 carbon atoms organized in a hexagonal or honeycomb lattice with π electron clouds. Being the thinnest materials ever created, a million times thinner than the diameter of a single human hair, it boasts the breadth of superlatives such as the strongest, lightest, best heat and electricity conducting material ever discovered.^[3–5] The story of graphene, the mother of all graphitic forms, started back in 1859 when chemist Benjamin C. Brodie first explained the highly lamellar structure of thermally reduced graphite oxide, the material formed by the addition of potassium chlorate to graphite slurry in fuming nitric acid.^[6,7] But the structure of graphite remained unidentified until 1916, and in 1947, P. R Wallace explored the theoretical existence of graphene. However, the pursuit of isolating graphene did not prove successful until 2004, when the scotch tape method involving micromechanical exfoliation of graphene layers was established by Prof. Andre Geim and Prof. Konstantine Novoselov.^[8] In addition to endearing the 2010 Nobel prize in physics, the discovery created an amplified research interest in graphene and graphene-related compounds and their applications.^[1,9–11]

Graphene can be synthesized in various forms. The synthesis method can enormously affect the type of graphene as the synthesis procedure can induce defects in the structure according to the second law of thermodynamics.^[1,2] However, some defects which can be controlled are proved to be beneficial for several applications. These defects in graphene structures can be divided into point defects and one-dimensional line defects. They could change the topology and affect the mechanical, thermal, and electrical conductivities. Lattice defects can break the integrity and symmetry of graphene crystals and hence can impact the property of electronic

transmission. At the same time, the gap formed by the defects can boost the interaction between atoms and graphene, which is beneficial for the application of graphene-based composites. There are two critical approaches to graphene production, they are bottom-up (BU) and top-down (TD).^[13] BU method uses carbon atoms as building blocks and may produce high-quality graphene.^[13,14] However, the amount of graphene formed is relatively small and hence can be used only for specific applications.^[13,15,16] In addition, this method is not appropriate for the production of graphene sheets with a large surface area and remains unsuitable for industrialization.^[16] Chemical vapor deposition (CVD) and Arc discharge are commonly used BU methods for graphene synthesis. The basic principle behind the TD method is to exfoliate graphite, which is used as the starting material. Graphite is merely a stack of graphene layers held together with Van der Waals forces. Mechanical or micro-mechanical exfoliation, Graphite intercalation, Nanotube slicing with carbon nanotube as a precursor, Pyrolysis, Reduction of graphite oxide, Electrochemical exfoliation, sonication, and Ball milling are various approaches that fall under TD method.^[16] In comparison with the BU method, the TD method is suitable for the large-scale production of graphene. TD method makes use of graphite as a precursor. Synthesis of pure natural graphite for graphene production requires high energy input and toxic solvents, and hence those production methods are classy or potentially environmentally hazardous. Moreover, natural graphite may not be a suitable option for graphene synthesis, as it contains natural impurities like silicate minerals, which can reduce the efficiency of graphene for specific applications. Besides, natural graphite has been classified as a critical resource by the European Union (EU), which indicates its high risk of supply shortage which could highly impact the economy.^[17] If we could make graphene from materials that would otherwise go to waste, the long-term price of graphene could be significantly reduced. The global demand for lithium-ion batteries (LIBs) is anticipated to upsurge from 185 GWh in 2020 to over 2,000 GWh by 2030.^[18] This rapid increase is to meet various emerging applications, mainly electric vehicle (EV) technology.^[19] This will create waste disposal issues in the near future, as these batteries reach their end of life. Battery reuse and recycling are gaining much attention to protecting the environment.^[20,21] Research on recycling technologies mainly focuses on high-value cathode materials, and only recently have researchers started working on anode recycling which constitutes 12%–21% of the total mass of LIB composition.

[a] M. L. Divya,⁺ Dr. S. Natarajan,⁺ Dr. V. Aravindan

Department of Chemistry
Indian Institute of Science Education and Research (IISER)
Tirupati 517507, India
E-mail: aravind_van@yahoo.com

[+] These authors contributed equally to this work.

An invited contribution to a Special Collection on Circular Economy

Graphite coating on the Cu foil can be easily removed, as the bonding force between graphite and Cu foil is weak. Recycling graphite can decrease the pressure of natural mining of graphite and alleviate the pollution caused by the spent anode.

Moreover, recovered graphite can be used to prepare high-value graphene, the building block of all graphitic materials. For the last few years, researchers have devoted more efforts to synthesize graphene from spent LIB graphite as it ensures a balance between scalability and quality in an economical way. This perspective discusses the current status, different methods available for graphene production from spent LIB graphite, and existing challenges and opportunities.

2. Graphite Oxide (GO) and Reduced Graphene Oxide (rGO)

Exfoliation of graphite can be done either physically or chemically.^[22,23] Graphite oxide (GO) is the material produced by oxidation of graphite, resulting in increased interlayer spacing with oxygen-containing functional groups such as epoxide, carbonyl, carboxyl, and hydroxyl groups on its basal plane. Due to the presence of these oxygen moieties, GO exhibits better interfacial interaction, mechanical and electrical properties for various applications.^[24] In contrast, the oxygen functionalization on GO reduces the electrical properties to an extent. Reduced graphene oxide (rGO) is produced by chemical or thermal reduction of GO to reduce the oxygen content. Thermal reduction is expensive as it requires high temperature, and hence chemical reduction is preferred by most researchers.^[24,25] Various reducing agents such as hydrazine hydrate, ascorbic acid, and others were reported in several studies. Chemical reduction of GO to rGO is the commonly used method for large-scale graphene synthesis. Graphite and graphene have unique properties, which might be restricted due to their hydrophobic nature. In contrast, GO and rGO exhibit high surface areas along with different properties and are hence suitable for electrode materials in batteries, supercapacitors, fuel cells, and solar cells. They are processible and can be self-assembled into macroscopic materials with precise compositions.^[22,26] In comparison with other graphene-related products, GO production can be easily scaled up, and hence it is suitable for energy-related applications.^[27] The rGO looks like graphene but contains residual oxygen, heteroatoms, and a certain degree of structural defects. Moreover, rGO can be made in the form of thin-film from an aqueous dispersion of GO in water and can be used for different applications such as in nanocomposite materials, in energy storage devices, in catalysis, in biomedical devices, and also as a surfactant.^[28]

3. Preparation of Graphene from Graphite

GO can be formed using graphite as a raw material by cost-effective chemical methods. The ground-breaking work on GO synthesis was reported in 1859 by Brodie in which he added

potassium chlorate ($KClO_3$) to a slurry of graphite in fuming nitric acid (HNO_3) at 60 °C with a reaction time of 4 days. Nearly 40 years later, in 1898, L. Staudenmaier modified Brodie's method by substituting two-thirds of HNO_3 with concentrated H_2SO_4 and adding $KClO_3$ in multiple aliquots during the course of the reaction, which could simplify the synthetic procedure by enabling the overall reaction in a single vessel. Approximately 60 years later, in 1958, the most important and broadly applied method of GO synthesis was introduced by Hummers and Offeman (Hummers method). In this alternate oxidation process, graphite oxidation was accomplished by the addition of potassium permanganate ($KMnO_4$) to a solution of sodium nitrate ($NaNO_3$) and sulfuric acid (H_2SO_4).^[6] Hummers method offered three critical advantages over earlier methods; such as 1) fast reaction, the reaction could be completed within hours; 2) replacement of $KClO_3$ with $KMnO_4$ and improved reaction safety by sidestepping the evolution of explosive ClO_2 , and 3) use of $NaNO_3$ instead of HNO_3 could evade acid fog formation. Though it has been paid extreme attention, it still has two significant drawbacks, such as 1) release of toxic gases like NO_2 and N_2O_4 during oxidation and 2) difficulty in removing residual Na^+ and NO_3^- ions from wastewater produced during GO synthesis and purification. Later in 2010, Tour and co-workers^[29] presented an improved Hummers method by excluding $NaNO_3$, increasing the quantity of $KMnO_4$, and performing the reaction in a 9:1 (by volume) mixture of H_2SO_4/H_3PO_4 . This modification resulted in increased reaction yield and reduced toxic gas evolution, and it used twice the quantity of $KMnO_4$ and 5.2 times H_2SO_4 in comparison with the Hummers method. In addition, the GO synthesized by the improved hummers method is more oxidized than that formed by the Hummers method.^[22,29–33] Reducing agents such as hydrazine, sodium borohydride, hydrochloric acid, and many more reduce GO into rGO. Melatonin, ascorbic acid, and polyphenol of green tea are examples of green reducing agents.^[34] However, the Hummers method requires a controlled reaction environment and produces sheet-shaped graphene layers with abundant structural defects that cause low electrical conductivity.^[13]

Liquid phase exfoliation (LPE) is another TD approach involving flaking natural graphite through sonication (cavitation) or high-shear mixing under mild operating conditions. High shear mixing is preferred over the sonication-assisted method for large-scale applications as this method can exfoliate graphite better than the LPE sonication method. The electrochemical exfoliation method depends on the type of anode, cathode, and electrolyte solution, and using graphite as anode, and it will be oxidized and subsequently exfoliated to produce graphene. The electrochemical method, in combination with sonication, can eliminate the requirement of high temperature and pressure. Laser ablation is another method with good advantages, such as being environmentally friendly and involving mild reaction conditions. Laser parameters should be controlled during the synthesis process and can affect productivity.^[13]

4. Benefits of Spent Graphite Over Natural/Synthetic Graphite

LIBs are becoming the leading source of power for portable electronics and also for EV technology. Producing battery-grade graphite for LIBs is energy exhaustive. Mining of natural graphite can cause dust emission; purification requires large quantities of sodium hydroxide and hydrofluoric acid, which are harmful to humans and the environment. For the assembly of one million EVs, ~75,000 tonnes of graphite is required.^[35,36]

However, synthetic graphite has started to rule the LIB anode graphite market due to its superior performance and cost-effectiveness in comparison with natural graphite. In order to meet the demand for graphite as active anode material for LIBs, a large quantity of graphite is produced and discarded after its retirement. The used anode graphite material can be effectively recovered from spent LIB instead of being sent to landfills as waste. Thus, recycling graphite can lessen the pressure on graphite mining and also could alleviate the environmental issues caused by the production process.^[36] Highly pure battery-grade graphite is expensive, nearly ten times higher than that of natural graphite. Recycling provides an inexpensive source of graphite. Moreover, due to weak bonding between Cu foil and graphite, graphite can be easily removed from Cu current collector.^[37,38] Graphite from spent LIB can also be considered as a cheap and ideal candidate for the high yield production of superior quality graphene.^[39] Even after repeated charge-discharge cycles, graphite anode retains a complete layered structure with oxygen-containing groups embedded into it and is conductive to prepare graphene.^[40] This used graphite has low ash content, perfect graphene layers with stretched *d* spacing induced by lithiation and de-lithiation during repeated charge-discharge cycles. Studies reported that used graphite is more prone to exfoliation in comparison with natural graphite.^[41] It shows irregular expansion along crystallographic *c*-direction due to Li-ion intercalation-de-intercalation during charge-discharge cycles. Battery cycling damaged Van der Waals bonds and thus minimized the interlayer bonding strength of graphite. To fabricate graphene and graphene oxide, it is essential to break the bonds and separate graphene layers. And hence, battery cycling can be measured as a pre-fabrication step, which can primarily improve the productivity of graphene and its derivatives.

Also, Graphene oxide from used graphite exhibited superlative homogeneity and electrochemical properties compared to that derived from pristine graphite. Zhang et al.^[43] reported that pre-expansion of graphene layers due to lithiation resulted in a 4-times increase in graphene productivity by shear mixing. With the addition of the acid, treatment step the productivity could be increased to 10 times higher than that from pristine graphite material. The decreased interlayer force between graphene layers could increase the sonication-assisted exfoliation efficiency of the used anode graphite to 3–11 times than natural graphite.^[39] Qiao et al.^[42] stated that the anode graphite has large layer spacing due to a reduction in interlamination force created by repeated charge-discharge cycles and pre-

pared 2D low-layer graphite flakes using freeze-thaw ultrasonic-assisted circulation method (Figure 1). Hence, it is easy to intercalate and peel. Reutilization of used graphite can provide an alternate source of graphite, reduce environmental pollution and encourage sustainable development of the anode graphite industry. Kruusenberg's group^[44] reported that even after a large number of lithiation-de-lithiation cycles in the batteries, anode graphite maintains its high quality, and graphene oxide can be effectively synthesized from it. Thus, battery cycling can be considered as a pre-fabrication step for graphite lattice expansion in the case of graphene production.

5. Graphene Preparation from Spent Graphite from LIBs

Graphene can be produced from the exfoliation of recovered graphite from spent LIBs by the TD method. Graphene layers are extracted or peeled either by the physical, chemical, or electrochemical method of exfoliation. Different approaches include mechanical cleavage using scotch tape, direct liquid-phase exfoliation of graphite or graphite intercalation compounds (GICs) by means of ultrasonication, and oxidation of graphite-to-GO, followed by ultrasonication to form graphene oxide and reduction to form rGO with restored electronic properties. As usual, Hummers method is mainly employed for the chemical reduction of GO. Graphene produced by direct exfoliation methods usually maintains high quality with low yield. These methods are being followed, along with some efforts to develop new routes for efficient and large-scale graphene synthesis. This section summarizes the different approaches taken by researchers for the synthesis of graphene from used recovered graphite.

5.1. Recovery of anode graphite from spent LIBs

The spent LIB anode comprised graphite powder, conductive carbon, binder (polyvinylidene fluoride, PVDF), and copper (Cu) film as the current collector.^[44] The anode graphite powder can be easily detached from Cu foil with the help of a scraper or tweezer, as it is loosely bound.^[40] Qiao et al.^[42] reported using a low-cost and environmentally friendly new organic deep eutectic solvent (DES) to separate graphite adhered to Cu sheet.^[45] Ribeiro et al.^[46] treated the graphite containing Cu foil pieces with concentrated nitric acid to solubilize Cu. Unlike natural graphite, anode graphite has organic and metallic impurities; treating with *N*-methyl-2-pyrrolidone (NMP), ethanol, and diluted water can remove these impurities.^[43] Ruan et al.^[47] reported thermal treatment (600 °C) to decompose binders and other organic pollutants followed by acidic leaching (H₂SO₄ & HCl) to eliminate metallic impurities. Other studies mentioned using de-ionized water to remove the Li-impurity and heating with dimethylformamide (DMF) to dissolve the binder.^[39,48] Calcination of anode graphite (at

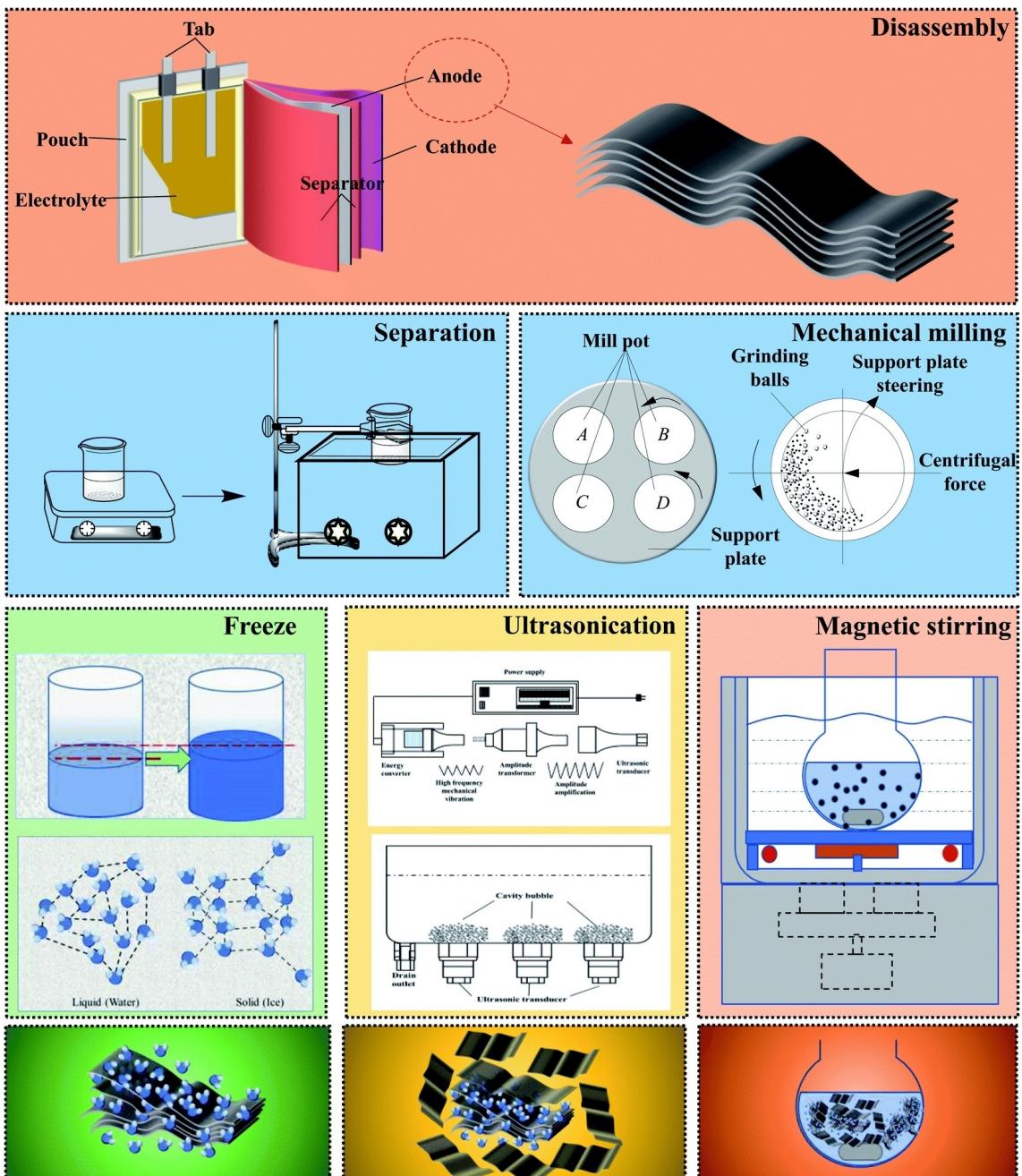


Figure 1. The scheme of the freeze–thaw ultrasonic assisted circulation method. Reproduced with permission from Ref. [42]. Copyright (2021) Royal Society of Chemistry.

600°C for 1 h) can be treated as an effective way to eliminate organic impurities from electrolyte and plasticizer.^[40]

5.2. Chemical methods for graphene oxide/graphene synthesis

In 2016, Badawy explored the synthesis of high-quality graphene oxide from the spent LIBs. Oxidation of anode graphite was done with the modified Hummers method, a combination of NaNO₃, KMnO₄, and H₂SO₄.^[6] The thus-formed

graphite oxide was reduced to graphene layers by ultrasonication. X-ray diffraction disclosed the absence of graphite peak (002) and the presence of (001) peak at 10.10°, corresponding to the formation of graphene oxide. The presence of epoxy, hydroxyl, and ketone groups of GO was established by Fourier-Transform Infrared spectroscopy (FTIR). In addition, SEM and TEM images also showed the formation of high-quality monolayer GO.^[49] In a similar study reported by Zhang et al.,^[40] spent LIB graphite was used to prepare graphene after oxidation to GO by simplified Hummers method, ultrasonic exfoliation to graphene oxide, and reduc-

tion using hydrazine hydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$) to yield graphene.^[50,51] The presence of oxygen-containing groups of anode graphite was identified by FTIR spectroscopy, along with benefits from intercalation reaction, which could lessen the consumption of oxidant in the GO preparation. After oxidation, the XRD spectrum of GO showed a peak at 10° and an expanded interlayer distance of 9.72 \AA . This increased interlayer distance is because of oxygen moieties along with water molecule intercalation in between graphene layers. The same concept was also confirmed from the I_D/I_G value of Raman spectra, which was shifted from 1.01 for anode graphite to 2.27 for GO. The authors stated that an increase in pH resulted in more OH^- , which caused the ionization of oxygen-containing groups. Thus, increased negative charges on the surface of GO created an enhanced force of electrostatic repulsion between graphene layers, which could favor the exfoliation of GO during ultrasonic separation. In addition, they also studied the effect of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ amount on GO reduction, and progressively converted into graphene with the addition of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ and was utterly transformed to graphene with $0.25\text{ mL N}_2\text{H}_4\cdot\text{H}_2\text{O}$. Due to the presence of oxygen-containing groups and structural defects in recovered graphite, the use of chemicals for graphene preparation could be reduced significantly compared to graphene preparation from natural graphite.^[40]

Zhao et al.^[41] fabricated soluble graphene sheets from spent LIB graphite through the modified Hummers method followed by deoxygenation using molten hydroxide salts ($\text{NaOH}/\text{KOH}=1/1$ eutectic). Ultrasonic exfoliation of GO was done in the presence of NMP, which disclosed that loosened graphene sheets in graphite are more prone to exfoliation. Molten hydroxide salts could effectively remove the unsaturated oxygen-containing moieties from exfoliated graphene oxide sheets while generating more hydroxyl functional groups at low temperatures ($<300^\circ\text{C}$). Higher temperature treatment of graphene oxide resulted in the removal of hydroxyl groups, and heat treatment at 220°C for ten hours produced graphene sheets with good solubility. Excellent solubility and dispersibility of reduced graphene sheets made it suitable for solution processing of graphene materials.^[41] Natarajan et al.^[52] prepared rGO from anode graphite in an eco-friendly manner using metallic cases (Aluminium (Al) and stainless steel (SS)) of spent LIBs as reducing agents in the presence of HCl at room temperature (RT) and 70°C . Graphene oxide was made through the Modified hummers method followed by exfoliation. Among the four different samples prepared (SSrGo-RT, SSrGO-70, AlrGO-RT, and AlrGO-70), AlrGO-RT exhibited high surface area and mesoporous nature with superior electrochemical performance. And it delivered a specific capacitance of 112 F g^{-1} with cyclic stability of 20,000 cycles. This study implied that such rGO could be considered for next-generation electrodes for building high-performance supercapacitors.^[52] Another work by the same research group^[48] reported the template-free synthesis of rGO entirely from mended graphite, using outer metallic Al cases as a reducing agent, and explored the gas (N_2 , H_2 , CO_2) storage capability. The specific surface area and total pore volume of synthesized rGO were calculated as $374\text{ m}^2\text{ g}^{-1}$ and $0.16\text{ cm}^3\text{ g}^{-1}$, respectively. Moreover, the H_2 uptake at

15 bar and 77 K and CO_2 uptake at 40 bar and 298 K were reported as 1.78% and 12%, respectively. This study shows the active synthesis of rGO from anode graphite without using any harmful reductants and possible gas storage applications.^[48]

Yang et al.^[53] proposed a new method to synthesize graphene from recovered graphite using an oxidation-reduction approach. Recovered graphite powder from spent LIB was converted into GO by the improved Hummers method. Chemical reduction of graphite oxide using vitamin C as a reducing agent resulted in the production of graphene. XRD analysis proved that most of the oxygen-containing functional groups from the surface of GO were removed during reduction by retaining its structure. In addition, the graphene prepared by this low-cost reduction method has a better-layered structure with fewer impurities and oxygen functional groups along with broader interlayer spacing and higher conductivity.^[53] Song et al.^[54] re-synthesized nano-structured LiFePO_4 /graphene composite derived from spent LIB via a novel closed-loop regeneration process. GO synthesis from recovered graphite was done through the Hummers method and was used for LiFePO_4 regeneration employing hydrothermal reaction. By compensating Li^+ into Li-deficient vacancy and reducing GO to form rGO simultaneously, high-performance $\text{LiFePO}_4/\text{rGO}$ composite was re-synthesized. The as-synthesized LiFePO_4 material with rGO coating displayed better electrochemical performance with low electrochemical impedance, smooth cyclic voltammograms, high capacity with flat voltage plateau, and high coulombic efficiency, cyclic stability, and rate capability. The XRD, XPS, ICP characterization studies revealed that the impurity phases and destructive crystals of both LiFePO_4 cathode and anode graphite were fixed during the hydrothermal reaction.^[54]

Li's research group^[43] proposed a lithiation-aided conversion of retired Li-ion battery anodes to graphene and graphene oxide. Anode powder collected from spent LIB displayed irregular expansion along the crystallographic *c*-direction via molecular dynamic (MD) calculations, as shown in Figure 2. Figure 2 revealed that Li-ion intercalation and de-intercalation during charge-discharge triggered the lattice expansion by damaging Van der Waals bonds and depressing the interlayer bonding strength in graphite. The synthesis of GO and rGO from graphite needs to break the bonds and separate graphene layers. The authors stated that battery cycling could be considered as a pre-fabrication step in preparing graphene from graphite, which could improve the productivity of graphene and graphene products. The effect of lithiation in GO and graphene synthesis was analyzed by synthesizing them from anode graphite and compared with that produced from pristine graphite. GO was synthesized from anode graphite by the simple Hummers method (avoiding low-temperature expansion of graphite), and that could exhibit excellent homogeneity and electrochemical properties. Further, the graphene production by shear mixing could result in a four times enhancement in productivity (Figure 3). Moreover, by introducing the acid treatment step, the graphene productivity was enhanced to 83.7%, which is ten times higher than pristine graphite powders.^[43] Kruusenberg's group^[44] presented a new

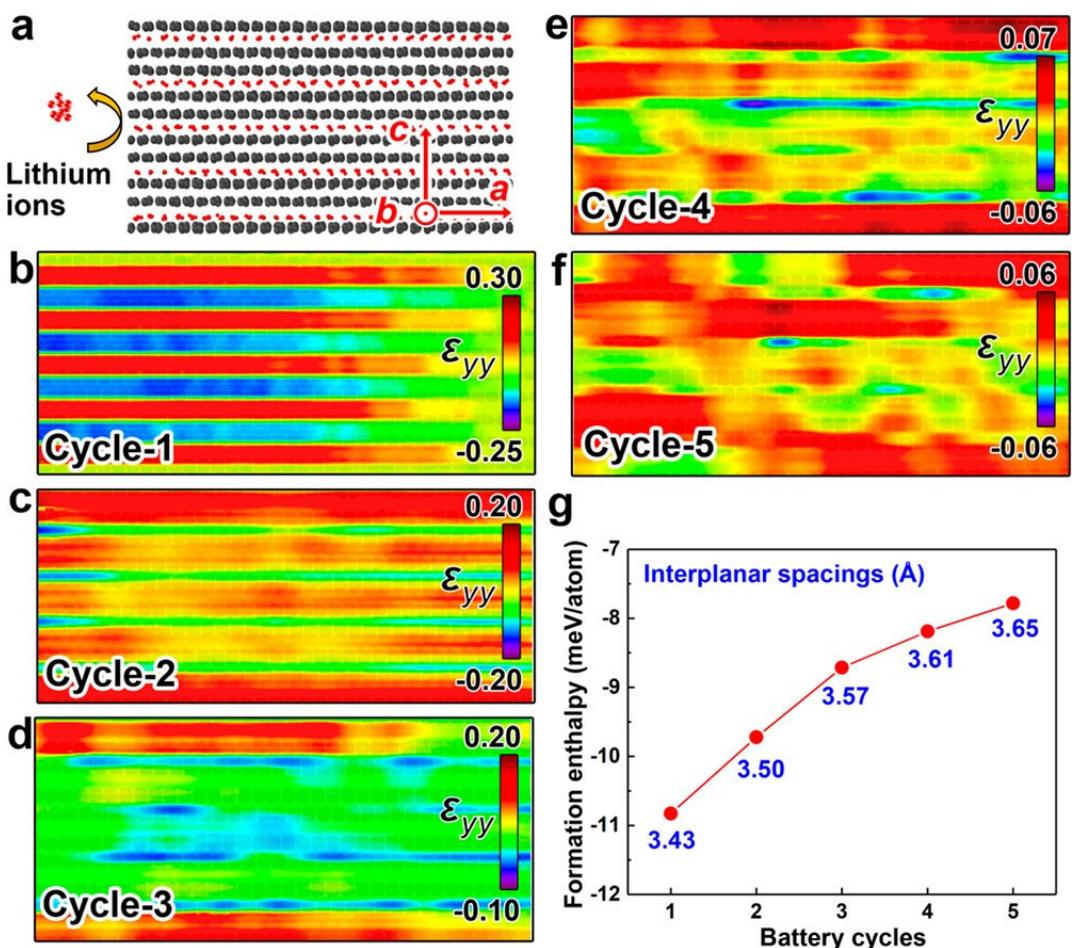


Figure 2. MD simulations of the lithiation/delithiation process in graphite during battery charge/discharge. a) Side view of the atomic structure of lithium-ion intercalated graphite compound (LiC_{12}). b–f) Lattice strain fields after each lithiation/delithiation cycle by coupling MD simulations and DIC. g) Formation enthalpy of bilayer graphite with various interlayer spacings at 0 K calculated by first principles. Reproduced with permission from Ref. [43]. Copyright (2019) American Chemical Society.

approach for recycling anode graphite by converting it into a valuable catalyst material for electrochemical oxygen reduction reaction (ORR). GO from anode graphite was made through the Modified Hummers method; after that, nitrogen doping was done by pyrolysis at 800°C in the presence of dicyandiamide to form nitrogen-doped graphene (NG-Bat). NG-bat was utilized as a catalyst material for ORR in alkaline media. The authors reported that spent LIB-derived NG-Bat exhibited superior physical and electrochemical properties than commercially available nitrogen-doped graphene.^[44]

In a recent study, Ribeiro et al.^[46] described the synthesis of hybrid materials based on rGO and cobalt oxide (CoO) from recycled LIBs. GO was synthesized from the anode graphite by the Modified Hummers method. Graphene oxide was obtained by ultrasonic exfoliation at room temperature for two hours. The GO solution was dried at 80°C to remove the excess water, and further, it was heat-treated at 450°C in a tubular furnace with a heating rate of $10^\circ\text{C min}^{-1}$ under Ar flow to form rGO. CoO produced by the hydrometallurgical route was combined with rGO using the sol-gel process followed by heat treatment to create the hybrid material, which showed promising proper-

ties as an electrochemical sensor of ascorbic acid in an aqueous solution.^[46] Ruan et al.^[47] reported a low-cost synthesis route for graphene nanosheets (few-layer graphene) from anode graphite for the first time. They optimized the oxidation approach given by Marcano et al.^[29] by introducing a 5:1 mixture of H_2SO_4 and H_3PO_4 and increased KMnO_4 , which resulted in enhanced oxidation efficiency compared to the typical Hummers method. Then high-quality few-layer graphene or graphene nanosheets were obtained via glucose thermal reduction and ensuing liquid exfoliation. Besides, nitrogen-doped graphene was synthesized with a simple chemical doping approach, which can be used as an oxygen reduction reaction catalyst in fuel cells.^[47] Yu et al.^[55] reported that the Modified Hummers method could be effectively used for impurity removal from recovered graphite and simultaneous conversion of it into 2D graphene oxide. In another study, Schiavi et al.^[56] proposed simultaneous production of rGO and Li–Mn-rich cathode material from spent LIB waste. Quantitative extraction of target metals (Co, Ni, and Mn) and oxidation of anode graphite to graphene oxide were concurrently achieved by the Hummers method. Recovered GO obtained by filtration

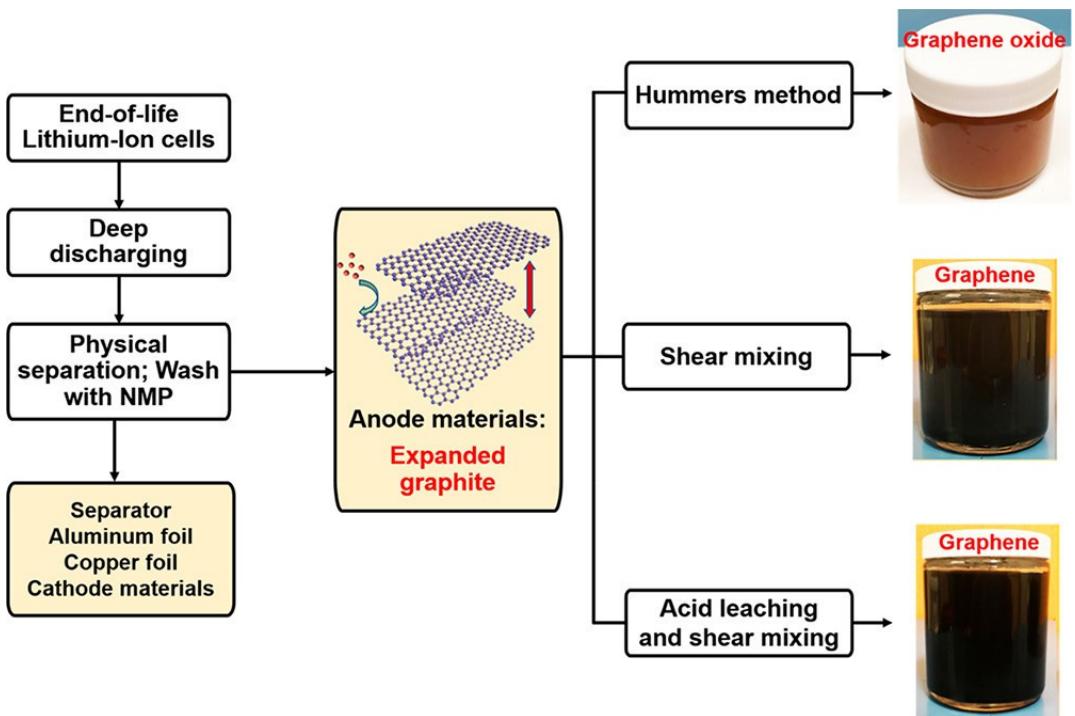


Figure 3. Schematic illustration of the proposed smart fabrication of graphene and graphene oxide from end-of-life batteries. Reproduced with permission from Ref. [43]. Copyright (2019) American Chemical Society.

was reduced to rGO by using ascorbic acid. In addition, they demonstrated that rGO productivity increases when the Hummers method is applied on anode graphite that has undergone lithiation/delithiation process during the battery life cycle.

The chemical oxidation-reduction process has been mainly used to produce graphene from the waste anode, graphite. However, due to large consumption of potent oxidizing and reducing agents and acids has raised environmental issues. The use of these chemical reagents is restricted in battery recycling mainly because of their high cost. Besides, the structural integrity of as-prepared graphene is interrupted as a result of disruption of hexagonally symmetric lattice due to chemical reactions.

5.3. Graphene from Li-graphite intercalation compound (Li-GIC)

GICs can be used as starting material for graphene synthesis by direct cleavage of bulk graphene layers. High-quality graphene can be attained from Li-GICs by means of Li metal or Li hydroxide as a source of intercalation. However, the high cost and high energy requirement for Li hydroxide melting remain a challenging factor in this case, whereas charged LIBs, in which Li occupies the vacancies between graphene layers, can be treated as a starting material for graphene synthesis.

Graphene production from Li-GIC has three main advantages, such as i) recycling of spent graphite, ii) graphene production with reduced cost, iii) recovery of active Li present

in Li-GICs, electrolyte, and in the SEI layer. Moreover, Li-ions in Li-GICs are highly active and hence can be easily extracted from spent LIB anode. However, two main factors need to be considered, such as the consequence of loss of recyclable Li-ion on Li-GICs formation and the economic viability of this production process. Zhang's group^[57] evaluated the appropriate state of charge (SoC) of spent LIB for Li-GIC preparation. The spent LIBs were recharged to form Li-GICs and were then subjected to hydrolysis and ultrasonication to form graphene via an expansion/micro-explosion mechanism. The SEM images of graphite showed the compact structure (Figure 4a and b). However, the graphene layers have been expanded for 60% SoC of graphite (Figure 4c). At the same time, a large expansion between graphene layers occurred but was not fully exfoliated for 100% SoC (Figure 4d). HR-TEM and SAED analysis further confirmed that the fully lithiated spent graphite was successfully converted into few-layered graphene with the hexagonal pattern (Figure 4g and h). After being charged to 100% SoC, the authors demonstrated that the graphite anode of spent LIB retained 50% of the original capacity and was wholly converted into Li-GICs (LiC_6 and LiC_{12}). 100% Li in Li-GICs, electrolyte and SEI layer was dissolved during Li-GIC exfoliation. The graphene formed was quantified as 58.8% 2–4 layered graphene and 41.2% of 1–2 layered graphene. Further, the study reported that the production method is economically viable with a low cost of \$540 per ton of graphene compared to commercial graphene.^[57]

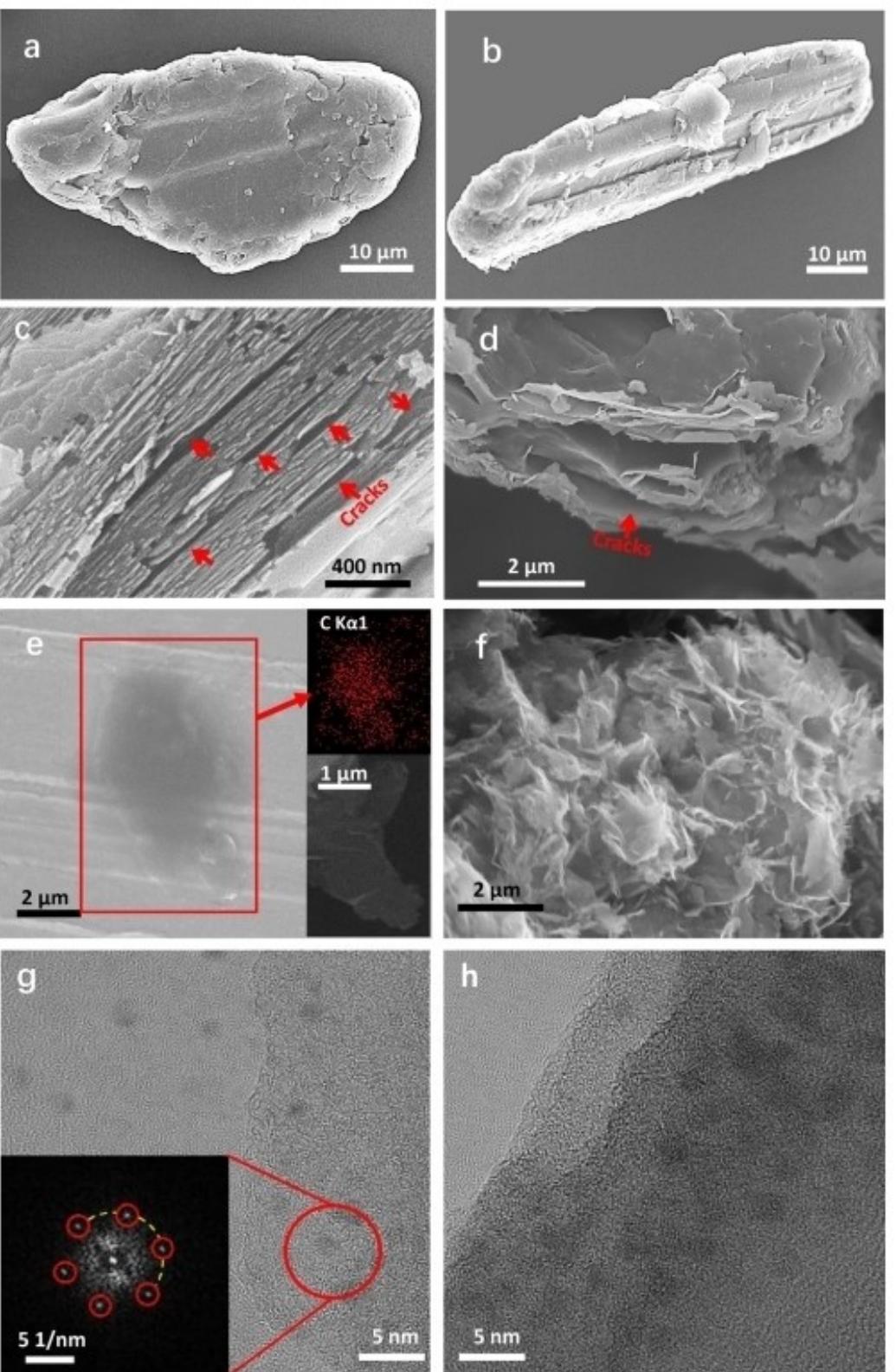


Figure 4. a, b) SEM and TEM images of lithiated graphite powder, c) prepared graphene from electrode of 60 % SoC, d) precipitated graphene from electrode of 100 % SoC, e-h) suspended graphene from electrode of 100 % SoC. Reproduced with permission from Ref. [57]. Copyright (2021) Elsevier.

5.4. Electrochemical exfoliation method

Chen et al.^[39] proposed a green and high yield method for synthesizing high-quality graphene by direct exfoliation of the recovered anode, graphite. They stated that anode graphite from LIB after repeated intercalation could be considered a cheap and ideal candidate for graphene production by the LPE. They explored direct sonication-assisted LPE of anode graphite in both an aqueous surfactant solution and a solvent mixture. The samples were exfoliated by horn sonication followed by centrifugation (Figure 5). Thin and free-standing graphene films (layer number 1–4) were formed by vacuum filtration. They conveyed that the exfoliation efficiency of used anode graphite is 3–11 times more than natural graphite, with the highest mass yield of 40%. More than 60% of as-produced graphene flakes exhibited a size of 1 mm with a thickness of 1.5 nm along with 9100 S m^{-1} conductivities. The authors also studied the potential application of thus formed graphene films in conductive ink preparation.^[39] In another study reported by Prakoso et al.,^[58] graphene flakes were produced by electrochemical exfoliation of anode graphite from spent Zn–C batteries. Exfoliation was done under varying DC voltages, using environmentally friendly poly (-sodium 4-styrene sulfonate), PSS surfactant solution of different concentrations. PSS was inserted into graphite interlayers to form C–S bonds and was confirmed by FTIR and XPS studies. High quality graphene flakes ($I_D/I_G = 0.86$, sheet resistance $R_s = 1.1 \text{ k}\Omega \text{sq}^{-1}$, transmittance = 89% at 550 nm) were obtained under an

applied potential of 5 V and 0.5 M PSS.^[34] These works illustrate electrochemical exfoliation as an effective and low-cost method for the exfoliation of anode graphite to form graphene.

6. Conclusion and Future Prospective

Undoubtedly, graphene has gained much attention in the last 2–3 decades due to its extraordinary combination of physical and chemical properties, including high specific surface area, thermal stability, mechanical strength, etc. made researchers analyze its prospective in many scientific fields such as nanotechnology, material science, engineering and even in biology too. Specifically, different preparation methods offer different properties for graphene, which has been explored in many applications such as electrodes for energy storage, as sorbents for wastewater and air purification, as well one can expand its application from flexible electronics to sensors also. However, graphene technology is mostly limited by its production, which is considered very expensive even though it is prepared from more abundant material graphite. However, the incredible evolution of graphene technology in numerous fields and scarcity of graphite in energy sectors build more demand for graphite in the market that push the researchers to find out alternative sources like spent LIBs. In this work, we have presented an overview of the recovery of graphite and preparation of graphene/reduced graphene oxide from the recycling of spent LIBs. Considering the estimated number of

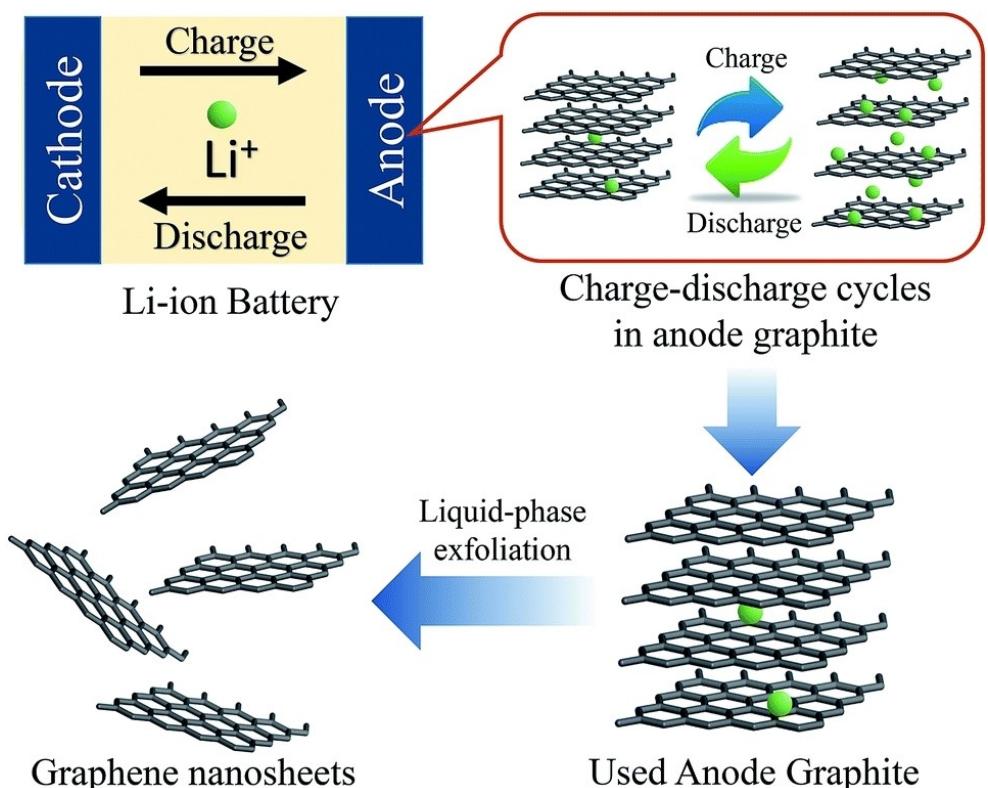


Figure 5. Illustration of the preparation of graphene with used anode graphite by liquid-phase exfoliation. Reproduced with permission from Ref. [39]. Copyright (2017) Royal Chemical Society.

spent LIBs worldwide, graphene can be prepared from the anode graphite part on an industrial scale that can answer the preparation of low-cost graphene by solving the environmental issues raised by spent LIBs.

Most of the graphene-based reviews have provided their viewpoints on the best methods for the preparation of graphene. But some barriers exist in the recycling of spent LIBs for the preparation of graphene oxide and graphene that should be overcome to achieve the goal of low-cost graphene while reducing pollution. Among the preparation of graphene from spent LIBs, shear-mixing is a scalable approach with good productivity while other techniques like chemical reduction are not environmentally friendly; electrochemical and high-temperature heat-treatment methods are generally energy-intensive. Using spent LIB components such as Al foil, and SS metallic cases can be used as reducing agents for the reduction of GO that can help to recycle all the components of spent LIBs along with reducing the cost for the recycling process; however, usage of acids in this process is problematic. Researchers/recyclers' efforts should be on the preparation of graphene via green synthesis routes using spent graphite which would be beneficial for producing a huge amount of GO, multi-layered graphene, and rGO from the freely available sources without harmful to the environment. In addition, graphene from spent LIBs is still lacking quality-wise; however, it is still usable for many graphene-based applications.

Very few reports confirmed the recovery of lithium from the SEI layer of the spent graphite before the preparation of graphene, which is formed during the charging-discharging cycles. Also, a unique procedure is required for the removal of metal impurities from the graphite if all components of spent LIBs are crushed together in the recycling process. Few reports indicated the elimination of the conductive additive and PVDF binder from the anode graphite before being used as a source for graphene/GO preparation. Most of the studies have not mentioned these impurities, which need to be understood well whether it has any possibility to influence the quality of graphene. Such efforts bring the quality preparation of graphene from waste sources and create the possibility for commercialization. Similarly, there is not much research on the evaluation of prepared graphene for energy storage applications, which material is currently dominating in this field owing to their extraordinary properties. Considering the current interests and ongoing sources demand, it is believed that the high-quality graphene with low-cost will be expected to emerge via effective and simple LIB recycling methodologies, especially in the fields of energy.

Acknowledgements

M.L.D. wishes to thank the funding through Women Scientist Scheme B (DST/WOSB/2018/2039) from the KIRAN division of the Department of Science and Technology (DST), Govt. of India. V.A. acknowledges financial support from the DST through Swarna-jayanti Fellowship (DST/SJF/PSA-02/2019-20) and Grant by Science and Engineering Research Board (SB/SJF/2020-21/12).

Conflict of Interest

The authors declare that they have no known competing interests

Keywords: anode · graphene · graphite · recycling · spent lithium-ion batteries

- [1] S. K. Tiwari, S. Sahoo, N. Wang, A. Huczko, *J. Sci. Adv. Mater. Devices* **2020**, *5*, 10–29.
- [2] M. J. Allen, V. C. Tung, R. B. Kaner, *Chem. Rev.* **2010**, *110*, 132–145.
- [3] T. Radadiya, *Eur. J. Mater. Sci.* **2015**, *2*, 6–18.
- [4] S. Trivedi, K. Lobo, H. S. S. Matte, **2019**, pp. 25–90 (doi: 10.1016/B978-0-08-102577-2.00003-8).
- [5] Y. Zhang, Z. Gao, N. Song, J. He, X. Li, *Mater. Today* **2018**, *9*, 319–335.
- [6] D. R. Dreyer, S. Park, C. W. Bielawski, R. S. Ruoff, *Chem. Soc. Rev.* **2010**, *39*, 228–240.
- [7] A. K. Geim, *Phys. Scr.* **2012**, *T146*, 014003.
- [8] A. K. Geim, K. S. Novoselov, *Nat. Mater.* **2007**, *6*, 183–191.
- [9] Y. Yan, F. Z. Nashath, S. Chen, S. Manickam, S. S. Lim, H. Zhao, E. Lester, T. Wu, C. H. Pang, *Nanotechnol. Rev.* **2020**, *9*, 1284–1314.
- [10] E. P. Randviir, D. A. C. Brownson, C. E. Banks, *Mater. Today* **2014**, *17*, 426–432.
- [11] A. K. Geim, *Science* **2009**, *324*, 1530–1534.
- [12] W. Tian, W. Li, W. Yu, X. Liu, *Micromachines (Basel)* **2017**, *8*, 163.
- [13] K. A. Madurani, S. Suprapto, N. I. Machrita, S. L. Bahar, W. Illiya, F. Kurniawan, *ECS J. Solid State Sci. Technol.* **2020**, *9*, 093013.
- [14] Y. Zhang, Z. Gao, X. Li, *Small* **2017**, *13*.
- [15] W. Choi, I. Lahiri, R. Seelaboyina, Y. S. Kang, *Crit. Rev. Solid State Mater. Sci.* **2010**, *35*, 52–71.
- [16] S. S. Shams, R. Zhang, J. Zhu, *Mater. Sci. Pol.* **2016**, *33*, 566–578.
- [17] J. Asenbauer, T. Eisenmann, M. Kuenzel, A. Kazzazi, Z. Chen, D. Bresser, *Sustain. Energy Fuels* **2020**, *4*, 5387–5416.
- [18] S. R. Department, <https://www.statista.com/statistics/1103218/global-battery-demand-forecast/>. Accessed July 23, 2021.
- [19] J. Y. Mo, W. Jeon, *Sustainability* **2018**, *10*.
- [20] Y. Zhao, O. Pohl, A. I. Bhatt, G. E. Collis, P. J. Mahon, T. Rüther, A. F. Hollenkamp, *Sustainable Chem.* **2021**, *2*.
- [21] G. Harper, R. Sommerville, E. Kendrick, L. Driscoll, P. Slater, R. Stolkin, A. Walton, P. Christensen, O. Heidrich, S. Lambert, A. Abbott, K. Ryder, L. Gaines, P. Anderson, *Nature* **2019**, *575*, 75–86.
- [22] J. Chen, B. Yao, C. Li, G. Shi, *Carbon* **2013**, *64*, 225–229.
- [23] K. S. Novoselov, V. I. Fal'ko, L. Colombo, P. R. Gellert, M. G. Schwab, K. Kim, *Nature* **2012**, *490*, 192–200.
- [24] N. M. S. Hidayah, W.-W. Liu, C.-W. Lai, N. Z. Noriman, C.-S. Khe, U. Hashim, H. C. Lee, *AIP Conf. Proc.* **2017**, *1892*, 150002.
- [25] J. Du, H.-M. Cheng, *Macromol. Chem. Phys.* **2012**, *213*, 1060–1077.
- [26] C. Li, G. Shi, *Nanoscale* **2012**, *4*, 5549–5563.
- [27] S. C. Ray, in *Applications of Graphene and Graphene-Oxide Based Nanomaterials* (Ed.: S. C. Ray), William Andrew Publishing, Oxford, **2015**, pp. 39–55.
- [28] A. Luedtke, in *Microelectronics & nano electronics*, Merck.
- [29] D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, J. M. Tour, *ACS Nano* **2010**, *4*, 4806–4814.
- [30] M. d. P. Lavin-Lopez, A. Romero, J. Garrido, L. Sanchez-Silva, J. L. Valverde, *Ind. Eng. Chem. Res.* **2016**, *55*, 12836–12847.
- [31] M. Sohail, M. Saleem, S. Ullah, N. Saeed, A. Afzidi, M. Khan, M. Arif, *Mod. Electron. Mater.* **2017**, *3*, 110–116.
- [32] N. I. Zaaba, K. L. Foo, U. Hashim, S. J. Tan, W.-W. Liu, C. H. Voon, *Procedia Eng.* **2017**, *184*, 469–477.
- [33] Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts, R. S. Ruoff, *Adv. Mater.* **2010**, *22*, 3906–3924.
- [34] E. Andrijanto, S. Shoelarta, G. Subiyanto, S. Rifki, *AIP Conf. Proc.* **2016**, *1725*, 020003.
- [35] G. e. N. letter, <https://goodelectronics.org/climate-change-impacts-of-graphite-production/>. Accessed on July 26, 2021.
- [36] S. Natarajan, V. Aravindan, *Adv. Energy Mater.* **2020**, *10*, 2002238.
- [37] S. Badawy, *Environ. Prog.* **2016**, *35*, 1485–1491.
- [38] S. Natarajan, M. Akshay, V. Aravindan, *Adv. Sustainable Syst.* **2022**, 2100432.

- [39] X. Chen, Y. Zhu, W. Peng, Y. Li, G. Zhang, F. Zhang, X. Fan, *J. Mater. Chem. A* **2017**, *5*, 5880–5885.
- [40] W. Zhang, Z. Liu, J. Xia, F. Li, W. He, G. Li, J. Huang, *Front. Environ. Sci. Eng.* **2017**, *11*, 6.
- [41] L. Zhao, X. Liu, C. Wan, X. Ye, F. Wu, *J. Mater. Eng. Perform.* **2018**, *27*, 875–880.
- [42] Y. Qiao, W. Sheng, C. He, B. Yang, H. Xu, C. Liu, Z. Rao, *Sustain. Energy Fuels* **2021**, *5*, 4882–4894.
- [43] Y. Zhang, N. Song, J. He, R. Chen, X. Li, *Nano Lett.* **2019**, *19*, 512–519.
- [44] K. Liivand, M. Kazemi, P. Walke, V. Mikli, M. Uibui, D. D. Macdonald, I. Krusenberg, *ChemSusChem* **2021**, *14*, 1103–1111.
- [45] Y. Qiao, W. Sheng, C. He, B. Yang, H. Xu, C. Liu, Z. Rao, *Sustain. Energy Fuels* **2021**.
- [46] J. S. Ribeiro, M. B. J. G. Freitas, J. C. C. Freitas, *J. Environ. Chem. Eng.* **2021**, *9*, 104689.
- [47] D. Ruan, Z. Zhang, X. Wu, L. Wu, F. Wang, K. Zou, K. Du, G. Hu, *Chem. Select* **2021**, *6*, 90–95.
- [48] S. Natarajan, H. C. Bajaj, V. Aravindan, *J. Mater. Chem. A* **2019**, *7*, 3244–3252.
- [49] S. M. Badawy, *Environ. Prog. Sustainable Energy* **2016**, *35*, 1485–1491.
- [50] R. Wang, Z. Wu, Z. Qin, C. Chen, H. Zhu, J. Wu, G. Chen, W. Fan, J. Wang, *Catal. Sci. Technol.* **2016**, *6*, 993–997.
- [51] H. Yu Huitao, B. Zhang, C. Bulin, R. Li, R. Xing, *Sci. Rep.* **2016**, *6*, 36143.
- [52] S. Natarajan, S. Rao Ede, H. C. Bajaj, S. Kundu, *Colloids Surf. A* **2018**, *543*, 98–108.
- [53] L. Yang, L. Yang, G. Xu, Q. Feng, Y. Li, E. Zhao, J. Ma, S. Fan, X. Li, *Sci. Rep.* **2019**, *9*, 9823.
- [54] W. Song, J. Liu, L. You, S. Wang, Q. Zhou, Y. Gao, R. Yin, W. Xu, Z. Guo, *J. Power Sources* **2019**, *419*, 192–202.
- [55] J. Yu, M. Lin, Q. Tan, J. Li, *J. Hazard. Mater.* **2021**, *401*, 123715.
- [56] P. G. Schiavi, R. Zanoni, M. Branchi, C. Marcucci, C. Zamparelli, P. Altimari, M. A. Navarra, F. Paganelli, *ACS Sustainable Chem. Eng.* **2021**, *9*, 13303–13311.
- [57] K. He, Z.-Y. Zhang, F.-S. Zhang, *Waste Manage.* **2021**, *124*, 283–292.
- [58] B. Prakoso, Y. Ma, R. Stephanie, N. H. Hawari, V. Suendo, H. Judawisstra, Y. Zong, Z. Liu, A. Sumboja, *RSC Adv.* **2020**, *10*, 10322–10328.

Manuscript received: January 25, 2022

Revised manuscript received: February 11, 2022

Version of record online: March 9, 2022
