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*Review Article*

# Graphene: Efficient Protective Coating Material for Current Collector in Energy Storage Devices

Satya Narayan Agawal<sup>1</sup>, Ashish Shrivastava<sup>2\*</sup>, Kulwant Singh<sup>3\*</sup> and Amit Soni<sup>4\*</sup>

<sup>1,4</sup>Electrical Engineering Department, Manipal University Jaipur, Rajasthan

<sup>2,3</sup>Skill Faculty of Engineering and Technology, Shri Vishwakarma Skill University, Palwal, Haryana

**\*Corresponding Authors:** Ashish Shrivastava, Kulwant Singh and Amit Soni

\*Email: [rewa.ashish@gmail.com](mailto:rewa.ashish@gmail.com), [eckulwant@gmail.com](mailto:eckulwant@gmail.com), [amit.soni@jaipur.manipal.edu](mailto:amit.soni@jaipur.manipal.edu)

## Abstract

Aluminium and copper foils are commonly used as current collectors due to low contact resistance, low price and high conductivity, in lithium ion (Li-ion) battery. Localized electrolyte corrosion during long-term cycling, weak bonding of the electrode material with the current collector and limited contact area are major issues still need to address. Advance level research is going on the above discussed paraments. This review study concentrated on employing graphene covering on copper and aluminum foil in lithium-ion batteries to address corrosion issues that the current collector was experiencing. Therefore, it is critical to commend the graphene coating on current collectors, such as copper and aluminum, for preventing corrosion and improving cycle performance while also extending their lifespan. This review study demonstrates that the graphene coating strengthens the bond between the electrode material and current collectors, which is critical for increasing power density. In addition, the modified graphene sheets behave as a protective layer against metal corrosion because of its hardness and mechanical strength can be treated as thin layer and also it offers high transparency and stability.

**Keywords:** Graphene, Aluminium, Copper, Current, Collector, Corrosion

**\*Author of correspondence: Email:** [rewa.ashish@gmail.com](mailto:rewa.ashish@gmail.com)

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## Introduction

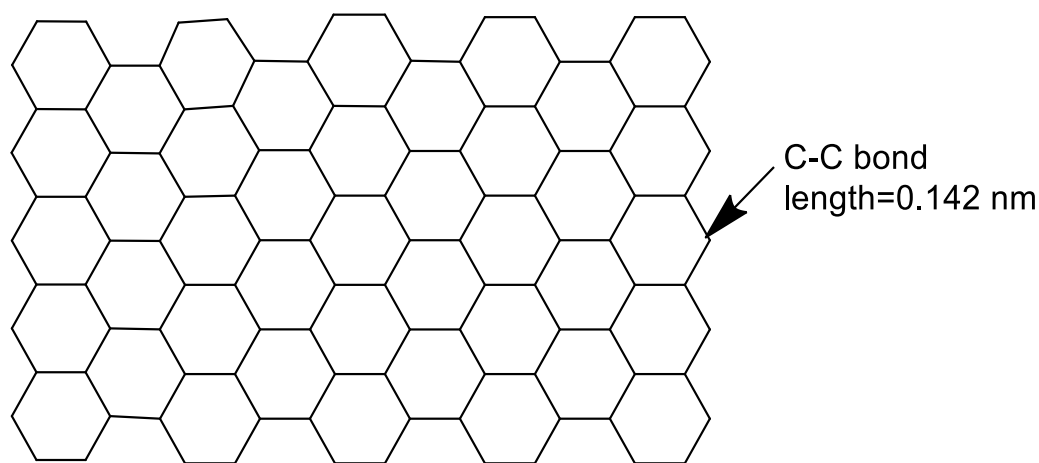
Per-capita electricity consumption has become the deciding factor about country's development. The total power demand is satisfied by using the hydrocarbon deposits like petroleum, crude oil, coal, and natural gas etc. The use of non-renewable fuels and their rapid depletion in recent years have caused a shift in research priorities towards the utilisation and exploitation of renewable energy sources, such as wind, solar, hydro, and tidal energy. But all the renewable energy sources are not available during whole year in every part of the globe. The concept of a word grid system and the storage

of renewable energy sources are offered by numerous powerful social figures as solutions to these issues. Energy conversion and storage methods require the use of renewable energy sources [1-5]. So, portable electric vehicles and hybrid electric vehicles have been established to meet the needs of our society. Hence, usage of fossil fuels is expected to have a significant economic and environmental impact in the future. In the development of society's progress and rising environmental concerns, the progress of low-cost and environmentally friendly new energy storage technologies is in need. Consequently, graphene is the

most preferred material for the fundamental energy storage component of electrochemical devices such as supercapacitors, flexible electronics, and solid-state batteries. Although the energy storage methods in these three systems are unique, they all share "electrochemical characteristics". These EES devices contains two electrodes which are linked with the electrolyte, and charge transfer is done in between electrode and electrolyte. Therefore, the electrode materials for all three systems must have the same qualities, such as high charge conductivities and chemical and electrochemical stability [6].

The lithium-ion (Li) battery, lithium air (Li-air) battery, Li-S battery, supercapacitor, and oxygen reduction reaction (ORR) are some of the most frequency used Energy Storage Devices (ESD). The primary subject of

this review article is the current collector for ESD based on graphene. Since Li batteries have long cycle life, voltage stability, high energy density, and low self-discharge rate, they have drawn the most attention in portable electronic devices like phones, cars, power tools, and hybrid electric vehicles, among other things. [7-9]. Similarly, Lithium sulphur batteries owned the natural abundance, less toxicity of sulphur, and it is inexpensive in its phenomenon. Furthermore, supercapacitor also received the advantages more than the batteries due to the good cyclability and high-power density. It is also known as electrochemical capacitor (ECs) as it is a very fast charging device or circuit and do not experience the memory effect so, it is considered as the application of renewable energy sources [10].



**Figure 1** Single layer graphene sheet

A single layer of graphene sheet, as shown in figure 1, densely packed in a honeycomb lattice structure attracted research interest due to its varied features [11]. It is wonder material that possess high intrinsic mobility, thermal conductivity, large specific surface area, Young's modulus, optical transmittance, and strong electrical conductivity with a current density of 108 A/cm<sup>2</sup> [12-18]. These properties of graphene, makes a material suitable for the coating on current collectors in Li batteries. In Li batteries, aluminium foil is used as cathode current collector, whereas anode current collectors made up of copper foil [19]. The current collector serves as an essential connection between the active materials, binders, and the conductive additives. To achieve the better electrochemical performance, reduce the resistance rate of the electrochemical system. As a result, the current collector's interface characteristic has a substantial impact on specific capacity, rate performance, and cycle life. To meet with the quick changes, the major focus is given on power density. Power density have the capability to increase the charging and discharging rates depends on anode and cathode materials, current collector (CC) resistance, and faradic reaction. In current collector, there are three basic problems which are

1. Anode and cathode material will corrode the current collector as the oxidation happen with the time.

2. The contact resistance between the current collector and anode and cathode is limited due to the electronic resistance and ionic diffusion resistance of active materials.

3. The bonding between the adhesion between cathode and anode material and current collector is limited which leads to the pulverization as the cyclicity increases.

So, to improve these problems in electrochemical energy storage devices, there are four basic needs for current collectors:

1. Graphene coating on copper current collector will enhance the cyclic stability of Li-ion.

2. It also enhances the discharge capacity of cell.

3. It reduces the electronic resistance and ionic diffusion resistance of active materials which leads to the improvement of power density.

4. It improves the contact resistance and adhesion between current collector which help in long life of cell i.e. reduce pulverization.

The innovative work of discovering the possibility to decrease the internal resistance and to improve the charge transfer kinetics of graphene film is achieved by Jiang et al. in 2016 [20]. They modified the copper foil to support spinel lithium titanate (Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>) anode directly by using LPCVD process. It improves the cycling rate at high current density and chemical stability. Taberna et al. [21] used electro-deposition to change the nano-architecture of a Copper (Cu) foil

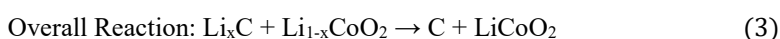
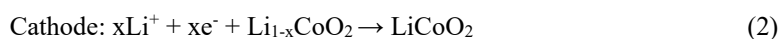
surface. Though high rate capacity and cycle life have been attained, large-scale manufacturing has been limited due to the high cost of anodized aluminum (AAO). Similarly, Kim et al. reported that the copper current collector enhanced the cyclic stability and discharged capacity of graphite anode layer by using the thin graphene film on the copper foil by using CVD process [22]. Likewise, Xu and group reported that by using the  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  (NCM523) cathode using graphene foil as a current collector i.e. NCM523/graphene foil, it shows the excellent stability, cyclicity, and energy density of the electrode. They reported at 0.5C, the gravimetric capacity is 137.3mAh/g that 44.5% higher than that of the NCM523/aluminum foil electrode [23]. Yu and co-workers [24] has reported the growth of lithium dendrites and facilitating uniform Li deposition utilizing reduced graphene oxide (rGO)@copper (Cu) foam as a current collector. The current density of reduced graphene oxide @Cu foam as an electrode and Li metal found to be  $1\text{mA}/\text{cm}^2$  with the high coulombic efficiency above than 98.5% after 350 cycles. Cheng et al. [25] in 2017 used the graphene-like-graphite (GLG) which is a carbon material as the anode material with a capacity of 608mAh/g and high rate capacity of Li ion battery. They showed that the lithium ions have been stored between the layers of GLG, and according to the NMR data for GLG at charging or discharging level, three types of lithium ions were found. Their results proved that the graphene-like-graphite is a potential carbon material for the future generation with the high capacity and quick charging for hybrid vehicles and electric vehicles. By using the graphene in lithium storage devices with all these research approaches, this review paper gives the idea about to improve the cycle rate, to reduce the internal resistance and the focus is given on power density.

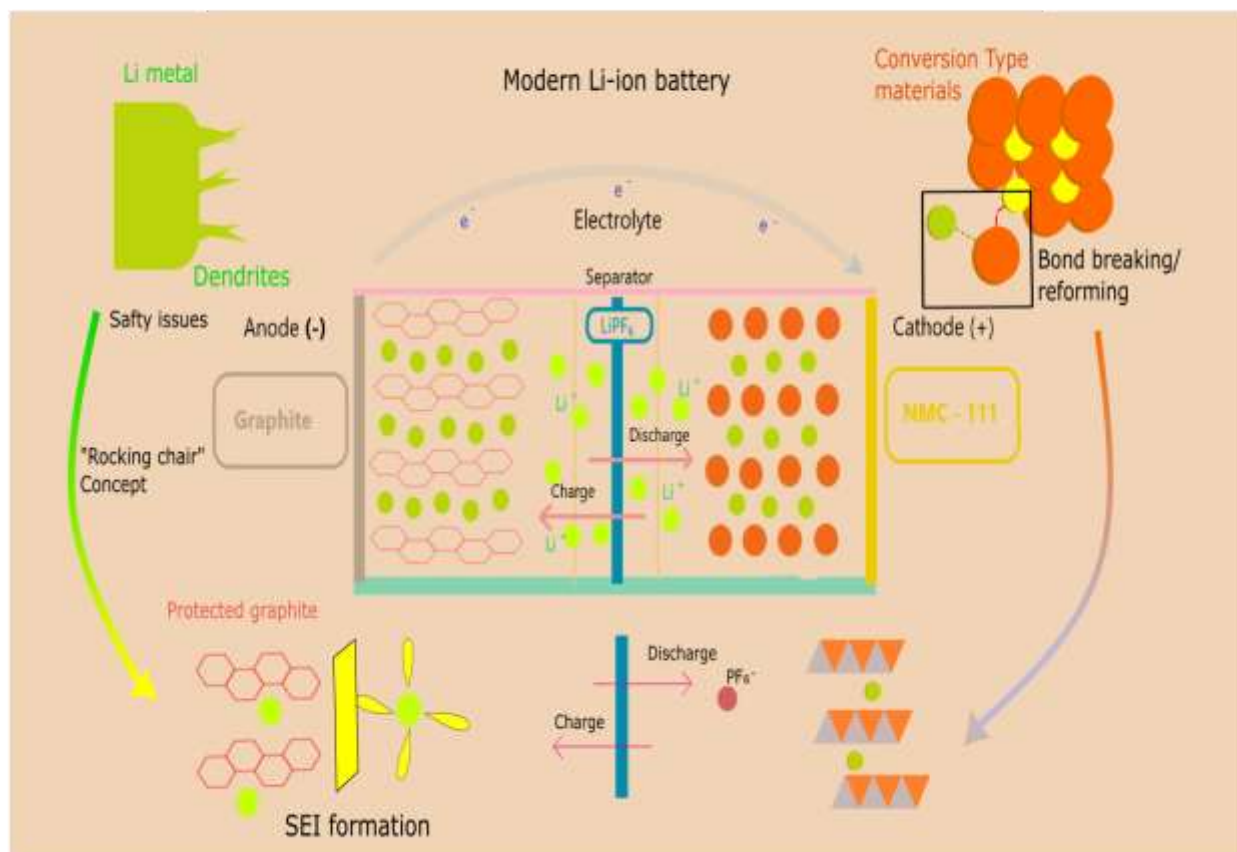
## 2. Principles of fast charging in Li ion

Current collectors are the most essential part which can highlighted the performance of lithium ion battery. Like, aluminum foils and copper foils have been selected as the best current collector for cathode and anode respectively. The problem of these two current collectors are the corrosion of aluminum current collector which can increase the internal resistance, self-discharge rate at a high potential, the micro-circuits made by the aluminum fragments under many cycles, high mass ratio

in battery, and weak bond between the electrode materials and current collectors. To improve these phenomenon, graphene has been taken as the promising candidate which includes its many unique properties like, it is the thinnest material which modifies the coated material without increasing its thickness. It has the good reinforcing mechanical strength of composite materials which enhance the strong nature. Further, high electrical and thermal conductivities, high surface area, sealing performance are the best properties for the practical applications. Researchers have used these characteristics of graphene to increase the charging capacity performance.

In lithium-ion cell, two electrodes having distinct electron affinities is used. In cell electrons travel from one electrode to another electrode, outer side circuitry. Whereas inside the cell the electrolyte ions closing the circuit. In this case, electrochemical reaction at the electrode converts the chemical energy into electrical energy. During discharging, lithium ions move from negative electrode to positive electrode. While in charging process, reverse process has been taken place from cathode to anode. In the whole process, electricity is passed through the metal current collector and the separator is used as an insulating material between anode and cathode [26]. Mostly, commercial cells are made up of lithium cobalt oxide ( $\text{LiCoO}_2$ ) cathode material and anode as a graphite [27]. Here, electrode active materials are mixed up with polymeric binder i.e. PVDF at the cathode and acetylene black which have the efficiency to improve the conductivity on the surface of current collector (CC). These slurries of anode and cathode material is respectively, coated on current collector. In charging, lithium ion moves from cathode to anode and accommodate in graphite which is used as anode material. While in discharging, lithium ion detached from graphite surface and back into the metal oxide. So, graphite is used as an anode material having low energy density [28]. Importantly, to know about the rate of battery i.e. charging or discharging is based on C-rate. The overall mechanism shows that the current collector transfers the charge to the external circuit, which can be explained using half-cell reaction on both electrodes [28]. These reactions are reversible in nature which proves that the battery is in rechargeable form. The reactions are [28]





**Figure 2:** Schematic diagram of lithium ion battery

In principle, the process of charging and discharging done by the insertion/deintercalation of Lithium ions transporting between the anode and cathode materials. Equation (1) gives the gravimetric energy density while equation (2) represent the volumetric energy densities and it can calculate the energy density of cell [28].

$$E_{\text{grav}} = \frac{\bar{V} \times Q}{\text{mass}} \quad (4)$$

$$E_{\text{vol}} = \frac{\bar{V} \times Q}{\text{Volume}} \quad (5)$$

$$\bar{V} = \frac{\int_0^Q V dQ}{Q} \quad (6)$$

Where,  $\bar{V}$  = average voltage,  $Q$  = charge

### Solid-electrolyte interface (SEI)

According to equation 7, lithium ion battery open circuit voltage ( $V_{\text{OC}}$ ) is depends upon electrode potential of cathode ( $\mu_{\text{C}}$ ) and electrode potential of anode ( $\mu_{\text{A}}$ ) [28]

$$V_{\text{OC}} = \frac{\mu_{\text{A}} - \mu_{\text{C}}}{e} \quad (7)$$

And, according to equation 8,

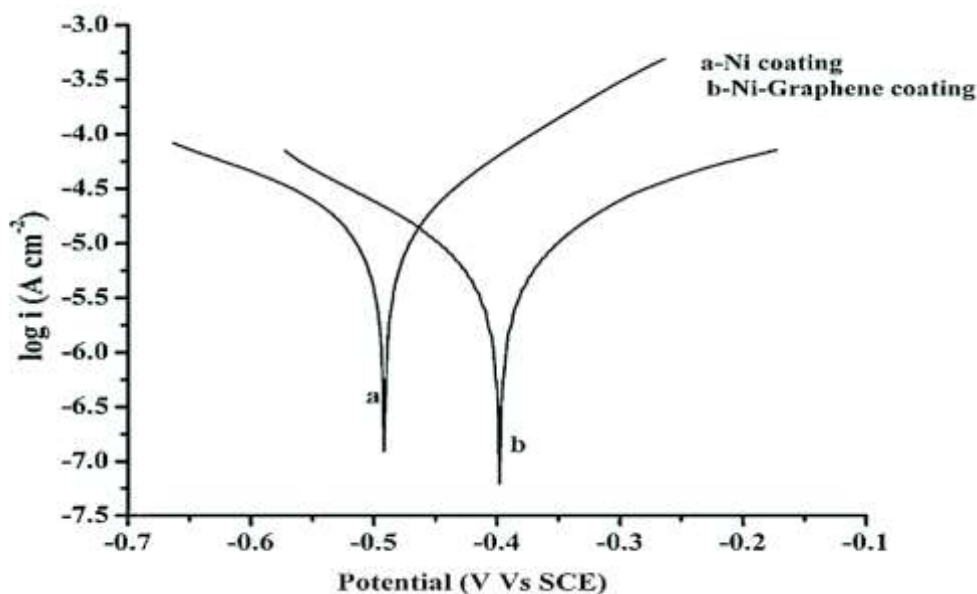
$$E_{\text{g}} = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (8)$$

If the electrolyte of LUMO (lowest unoccupied molecular orbital) is lower than electrode potential of anode ( $\mu_{\text{A}}$ ), then it reduced electrochemically. While, if the HOMO (highest occupied molecular orbital) of the electrolyte is greater than electrode potential of cathode ( $\mu_{\text{C}}$ ), then it gets oxidised. So, in commercial voltage,

non-aqueous electrolyte has a high  $E_{\text{g}}$  to enlarge the cell voltage and energy density also [27]. The electrode potential of anode of graphite anode or lithium metal lies below the LUMO of non-aqueous organic electrolyte [29]. This electrolyte depends on the passivation layer which is known as SEI (solid-electrolyte interface) [30].

### 3. Methods of Graphene coating on current collectors

It is well known that graphene serves as the foundation for all graphite materials. Graphene used to make coatings against metal corrosion, it shows transparency in nature having thermal stability around 400°C [31]. As single-layer and multilayer graphene films both are transparent and around 90 percent transmittance for four layered graphene, and also by spreading over on the graphene coating on metal substrates, it provides oxidation resistance [32, 33]. Graphene's large surface area and non-polar carbon structure make it a hydrophobic substance that shields metals from deterioration. [34-35]. Kumar and group [36] studied the corrosion prevention capabilities of the manufactured composite by depositing nickel (Ni) graphene coating on a carbon steel substrate. As shown in Figure 3, it increases the micro hardness of material, not only the corrosion resistance. Coating of graphene on the current collector, makes it more useable for long time.



**Figure 3: Tafel curves by Nickel coating and Ni-graphene coatings in 3.5% sodium chloride solution [36]**

Table 1 shows numerous possible processes for making graphene-based protective coatings that may be used to prevent corrosion, flame/irradiation, bacterial development, and cut. Dry processing and wet

processing are the two procedures have varied degrees of utility depending on the sensitivity of the medium and application [37].

Table 1 Possible processes for making Graphene-based protective coatings			
Coating method	Schemes	Concepts	Reference
Dry processing	CVD	The reactant gases are methane ( $\text{CH}_4$ ) or ethyne ( $\text{C}_2\text{H}_2$ ) mixed with argon (Ar) and hydrogen ( $\text{H}_2$ ) in a CVD reactor about $1000^\circ\text{C}$ to create a corrosion-resistant Graphene layer.	[31], [32]
Dry processing	Rapid thermal processing	On metal substrate, organic compounds like naphthalene ( $\text{C}_{10}\text{H}_8$ ), coronene ( $\text{C}_{24}\text{H}_{12}$ ), anthracene ( $\text{C}_{14}\text{H}_{10}$ ), and polyacrylonitrile ( $\text{C}_3\text{H}_3\text{N}$ ) <sub>n</sub> at $1000^\circ\text{C}$ forms the multilayer graphene like coating. With acetone at $1000^\circ\text{C}$ Rapid thermal annealing on a pre-annealed Copper foil can provide a corrosion-resistant graphene coating (RTA)	[33], [34]
Dry processing	Powder spray	A plasma generating gas is delivered to the graphene ceramic composite powder at high temperature and deposited at high velocity.	[35]
Wet processing	Drop casting	Drops of graphene oxide (GO) solution applied to a surface coated with a cation surfactant, followed by air drying or oven drying to create homogenous films.	[36]
Wet processing	Dip coating	A dispersion of graphene oxide absorbs the substrate.	[37], [38]

### 3.1 Effect of graphene coating on Anode current collector

Due to its thermally stable nature, one atomically thick material, gas-impermeable, graphene can be used as the best material for the coating on copper foil as it enhanced the active surface area, reduced adhesion, friction, and wear when coated on the surface to extend the longevity of the devices [46-50]. Wang et al. reported that the graphene layers increases the load carrying capacity, and

decreases the friction. For monolayer graphene, bi-layer graphene and trilayer graphene, the friction coefficient noted were 0.24, 0.18, and 0.11 respectively [51]. Likewise, Secondary electron yield (SEY) and secondary electron energy spectra have been taken for the determination of graphene coating on Cu foil. It resulted into the value of SEY decreases from 2.1 to 1.5 by Cao et al. in 2016 [52].

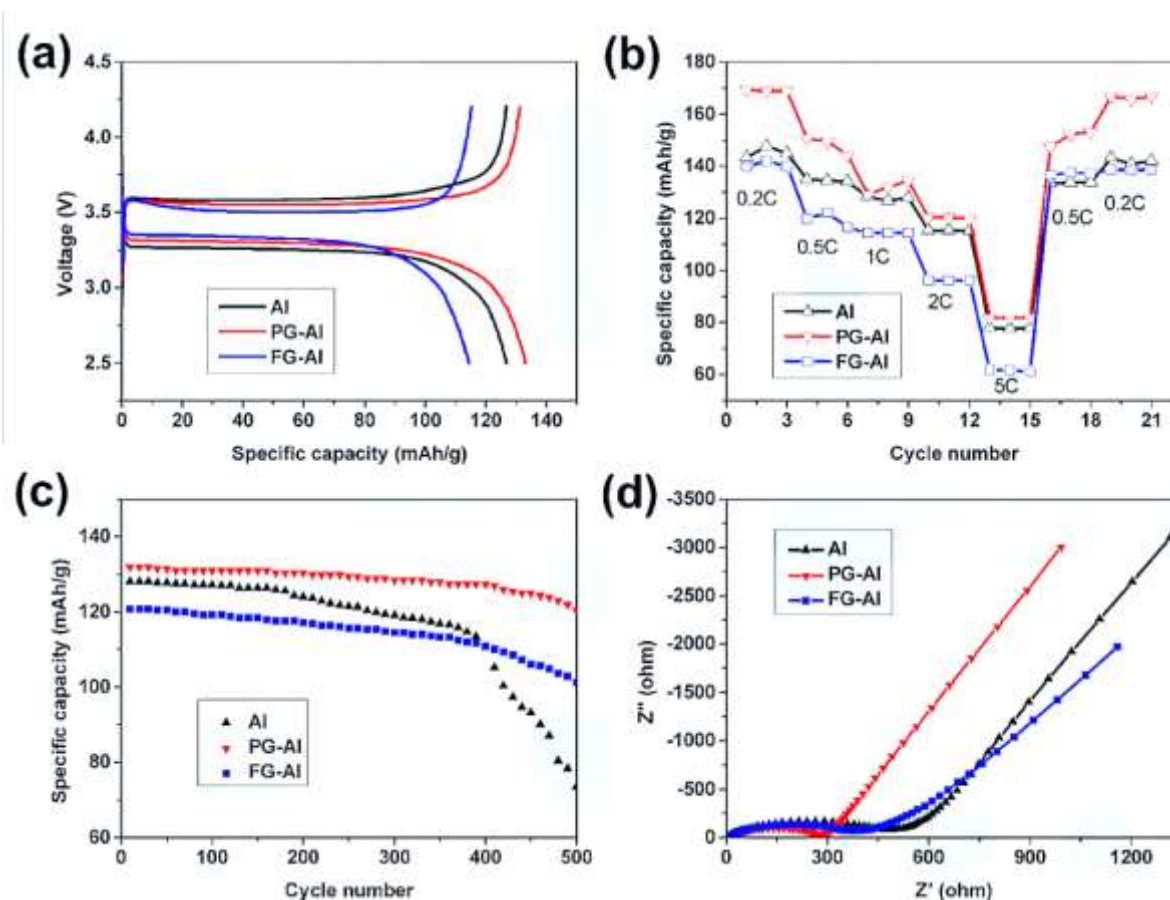
**Table 2: Various materials and techniques used on anode current collector**

S. No.	Material	Techniques	Characteristics	Reference
1	Graphene/Cu (111)	Monolayer- 0.24 Bilayer- 0.18 Trilayer- 0.11	Increase low friction range Decreases the friction	[51]
2.	Graphene coated copper foil	Secondary electron emission yield (SEY)	Increase surface potential barrier	[52]
3.	CuO/Graphene coated	----	Slow down the oxidation process	[53]
4.	Graphene/Cu	-----	Increase separation rate	[54]
5.	Graphene/Cu	-----	Long-term oxidation of copper	[55]

### 3.2 Effect of graphene coating on cathode current collector

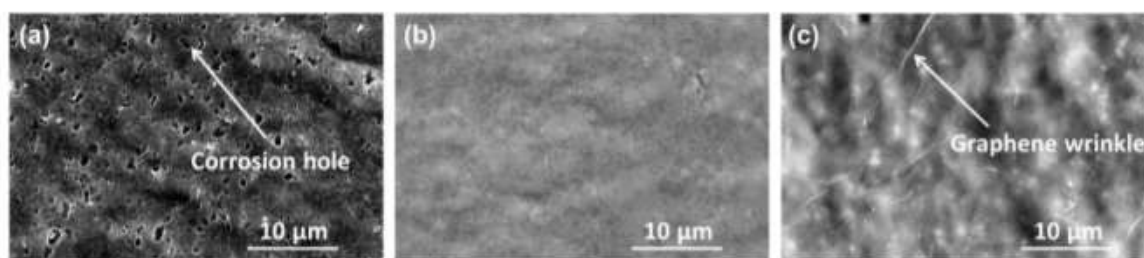
Though aluminium (Al) foils are used as a cathode CC for energy storage devices. Hence, it suffers a lot of challenges such as less adhesion with electrodes, localized corrosion with electrolytes during cycling [56]. So, graphene coated aluminium foils behaves as the best solution for the current collectors (CC) for Li-ion batteries. In this regard, Wang et al. in 2019 [56] reported that the carbon black modified Al foil improved the electrochemical performance in terms of resistance

rate, long term cycling. They also concluded that the coating of graphene nanosheets increase the adhesive strength between the electrode and CC and also increases the contact area. The interpretation of both properties shown in figure 4 and 5 [56]. The electrochemical performance of Li-ion battery when LFP used as cathode material with aluminum current collector, some part of aluminum coated with graphene (PG-Al), and whole part of aluminum current collector coated with graphene in figure 4.



**Figure 4. (a) Lithiation and Delithiation at the rate of 1 C. (b) The specific capacity vs cyclicality at different charging rates (c) stability in the cyclicality at 1 C. (d) impedance before charge and discharge test [56].**

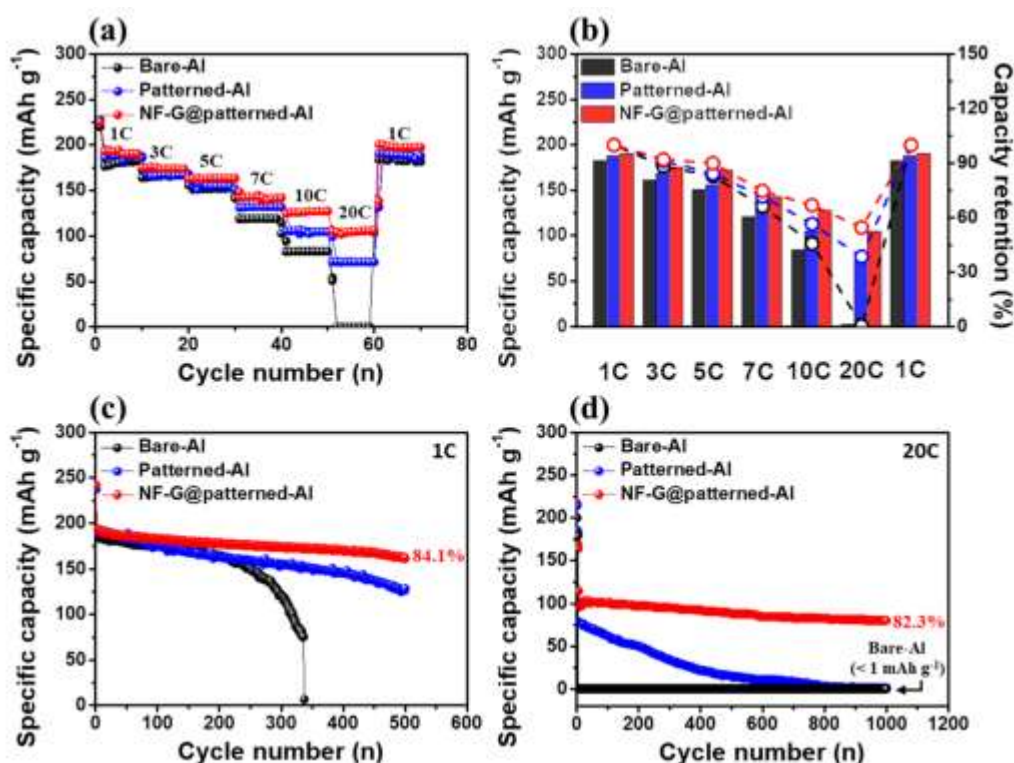




**Figure 5.** High magnification SEM images after 500 cycles ( $\times 10K$ ) (a) bare Aluminium, (b) partially coated graphene aluminium sheet PG-Al (c) fully coated graphene aluminium sheet FG-Al [56].

Zhao and group also fabricated aluminum current collector in which graphene coating is done by using the AlSi10Mg alloy by a selective laser melting process (SLM) [57]. It improves the growth rate of graphene on aluminum which was responsible for the refining of cell. Shin and group used the heteroatom doped graphene layer on aluminum foil to increase charging and the cyclicality of lithium ion battery. They noted after thousands cycles, the specific capacity is 87.1mAh/g with the retention of 82.3% at 20C after 1000 cycles

[58]. The improvement in the cyclicality at higher charging rate is due to improvement of contact area between cathode material and current collector. Similarly, shin and group [58] also reported that NF-G doped current collector shows improve cyclicality, stability and charging rate at ultrafast charging. On the other hand, it has been also observed long life of electrode due to improvement of contact area between current collector and electrode (Figure 6).



**Figure 6.** Performance measurement of current collector when it is Bare-Al, Patterned – Al, and NF-G@patterned-Al (a) measurement of specific capacity at different current densities; (b) estimation of capacity retentions and specific capacity; (c) and (d) short cycling test at 500 cycles and long cycling test at 1000 cycles.

Table 3 Various materials and techniques used on cathode current collector				
S. No.	Material	Techniques	Characteristics	Reference
1	G-Al/ LiFePO <sub>4</sub>	-----	Improves long term cycling	[56]
2.	AlSi10Mg	selective laser melting process (SLM).	Increase fast charging and cyclicality	[57]
3.	Heteroatom-Doped Graphene Layer	----	Long term cycling	[58]

#### 4. Corrosion

Metal corrosion is defined in which substrates of metal are degraded by chemical interactions or electrochemical interactions. Corrosion is a serious problem as it has the potential to cause significant economic losses and catastrophic harm in a variety of domains in everyday life and industry worldwide [59]. Corrosion becomes the problem in many sectors nowadays, and as a result, material corrosion prevention has gotten a lot of attention. Even though major research efforts have been made to create innovative corrosion prevention technologies, there is still a pressing need to improve component longevity. Coating various nanocomposite types, hydrophobic materials, and organic-inorganic hybrids has extended the life of items susceptible to oxidation and corrosion while also saving a substantial amount of money. [60-65]. Hence, Graphene is commonly used as a filler in the production of coatings on current collector against corrosion.

##### 4.1 Corrosion of copper current collector

Copper (Cu) have been extremely important in the manufacturing process of battery cell because of its remarkable qualities, which include high electrical conductivity and thermal conductivity.

Prior studies have revealed that the protective hydroxide or copper oxide (CuO) layer develops on the copper surface at neutral pH values [66]. The creation of an

oxide or hydroxide layer has the ability to slow down dissolving and reduction processes. The diffusion of corrosive elements on metal substrates is limited which protect them from corrosion and it can improve their mechanical qualities by coating of copper with an anti-corrosive layer [67]. Coating of Graphene on copper foil behaves as an excellent anti-corrosion material [68].

Reference [69] reported that multilayer graphene grown using CVD for 3 hours at 500°C and and wet chemical by 31% H<sub>2</sub>O<sub>2</sub> for 2 h shows anticorrosion effect to nickel from air oxidation. Similarly in reference [70] graphene-coated Ni and Cu substrates exhibit that graphene coated layer reduces corrosion rate and it can provide the barrier to metal dissolution from metal substrate to the environment.

Likewise, Singh and team synthesized graphene-oxide polymer composite (GOPC) by using electrophoretic deposition (EPD) process on the surface of Cu current collector which prevent copper current collector from oxidation and corrosion. Both potential dynamic polarization and EIS data were used to create the GOPC composite covering in order to prevent copper against corrosion under extreme conditions (Figures 7 and 8). This methodology resulted into the less expensive, less time consuming and facile [71]. Hence, graphene helps to survive in corrosion behaviour by increasing the area, size, improving the resistance, reduces the thermal oxidation.

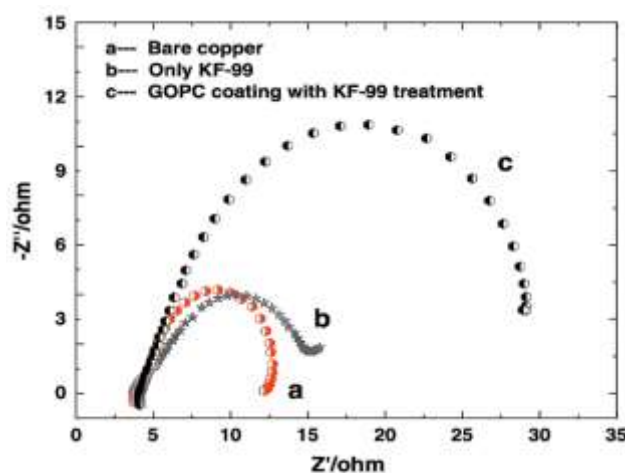


Figure 7: Explaining the Electrochemical impedance spectra of coating on copper plate (a) only copper, (b) Cu coating with only KF-99, (c) GOPC coating with KF-99 treatment [71].

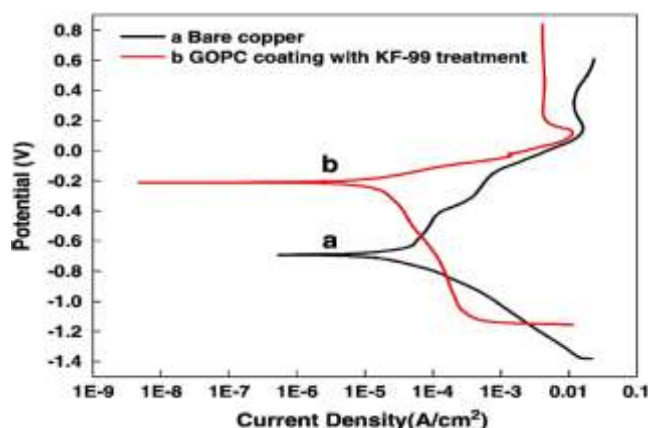


Figure 8: The tafel plots of GOPC coating with KF-99 treatment and bare copper [71]



#### 4.2 Corrosion of aluminium current collector

Aluminium has exceptional corrosion prevention capability even in aqueous media because the oxide coating produced on the aluminium surface is strong enough to prevent from the corrosion [72]. Another form of corrosion that Al can experience is pitting corrosion, which occurs most frequently in environments containing  $\text{Cl}^-$  ions. Hence, Pits are generated of  $\text{Cl}^-$  penetrating and diffusing through the oxide layer, resulting in the creation of aluminium chloride complexes. Because of the continued build-up of aluminium chloride, the protective layer deteriorates, resulting in the formation of pits [73, 74]. Chromium (Cr)-based coatings have been widely used to preserve aluminium composites due to their exceptional corrosion prevention capability. Furthermore, the usage of hexavalent chromium compounds is thought to be

harmful to human health and the environment [75, 76]. However, environmental pollutants such as hexavalent chromium species are present in these preventive approaches. So, graphene considered as the best source for the corrosion protection coating in applications includes aircraft, microelectronic component etc. [77, 78]. Some studies show that coatings of graphene have been prepared by CVD technique. Hikku and group [79] designed the graphene melt polyvinyl alcohol (G-PVA) nanocomposite which shows effective corrosion resistance for Aluminum-2219 foil as shown in figure 9. In a 3.5% NaCl solution, Al-2219 exhibits a 45.25 mpy corrosion rate that drops to 2.576 mpy for PVA and  $3.853 \times 10^{-4}$  mpy for G-PVA coated Al-2219.. The results show the GPVA coated Al have the better corrosion resistant then bare Al in as shown in figure 9.

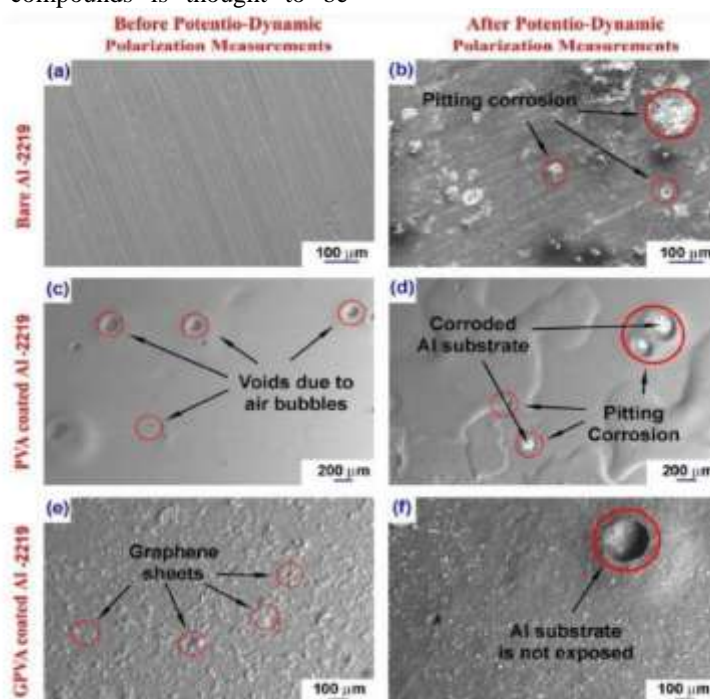


Figure 9. Potentiodynamic polarization measurements are shown in the SEM image of Al-2219, PVA and GPVA coat [79]

In figure 10 electrochemical impedance spectra of bare, PVA coated Al and GPVA coated Al. The electrochemical impedance (Nyquist plot) for the bare and PVA-coated Al-2219 in 3.5% NaCl is shown in Figure 10a. Furthermore, the Nyquist curve for GPVA

coated Al in figure 10b displays Warburg impedance rather than an inductive loop in the low frequency range. The bode magnitude and phase angle plot for bare and coated Al-2219, as obtained from the EIS analysis, is displayed in Fig. 10c [79].

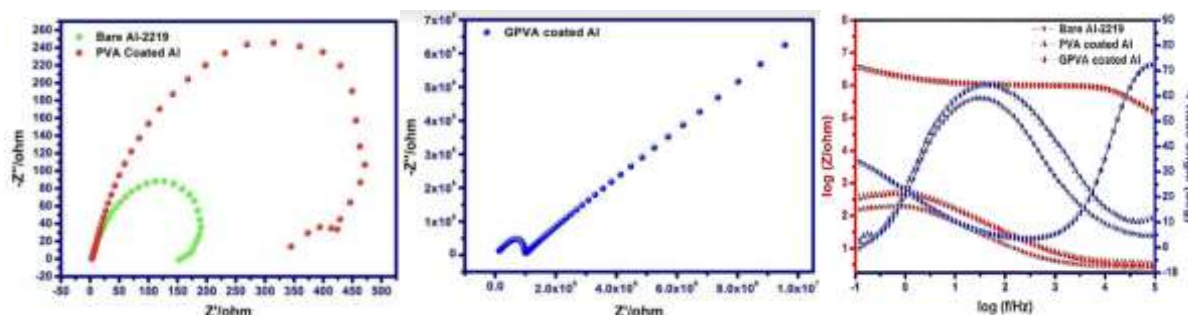


Figure 10: GPVA coated Al-2219, Bare Al-2219 and PVA coated Al-2219 and Bode plot [79].

Reference [73] produced a graphene coating for aluminium surfaces to prevent corrosion by using a dip coating method in a 0.5 M sodium chloride solution. Through the use of Raman spectra, they were able to determine that the coating on the aluminium surface was

uniform and sequential. Figure 11 illustrates that the resistance was raised around three times. The graphene oxide Raman spectra show a D peak at about  $1350\text{ cm}^{-1}$ , an intensity ratio (D/G) of 0.95 between the D and G peaks and a graphene peak at around  $1580\text{ cm}^{-1}$ .

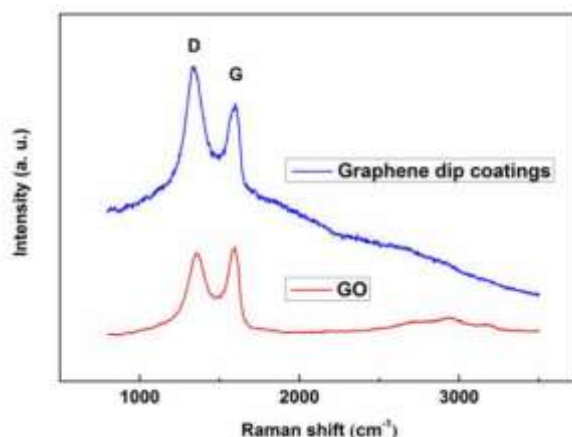


Figure 11. Graphene oxide and graphene dip coatings' Raman spectra [73]

### 5. Effect of graphene in Li-ion cell chemistry

Lithium-ion cell suffer the problem of low power density, because of its high charge/discharge rate. The major reasons of high polarization are poor Li-ion diffusion rate, thermal and electrical conductivity at the electrolyte and electrode interface. Therefore, it become necessity to add or synthesize new electrode materials that exhibit a large surface area, porous structure, high electrical or thermal conductivity, and a short ionic diffusion path. Graphite is a developed as an anode material with high columbic efficiency and great cycle performance. During charging, lithium ions intercalate into graphite, forms lithium carbide ( $\text{LiC}_6$ ). Graphite has a specific capacity is  $372\text{ mAhg}^{-1}$ .

Material having high specific capacity are required to improve the performance of li-ion batteries [80]. Carbon nanomaterials [81], fullerenes [82], mesoporous carbon [83] have been used in the lithium-ion batteries. Metals, metal oxides, and metal nitrides, in addition to carbon nanomaterials, were investigated for improvement in Li-

ion battery technology in place of graphite [84, 85]. Graphene has also been employed as an additive for both cathode [86] and anode [87] with excellent success.

Report produced by Kudo and team shows specific capacity from  $540\text{ mAhg}^{-1}$  for rGO to  $730\text{ mAhg}^{-1}$  as combination of carbon nanotubes (CNT) and carbon 60 ( $\text{C}_{60}$ ) into the reduced graphene oxide (GO) [88]. The electron affinity of carbon nanotube and  $\text{C}_{60}$  discussed about the electronic charge in graphene and the d-spacing increases from 0.37 to 0.43 nm of CNT and Carbon 60 in which both help lithium ion intercalation. Pan et al. reported the disordered graphene sheets which can be used for anode lithium ion battery and having high capacity about  $794\text{--}1054\text{ mAhg}^{-1}$  [89].

It has been noted that the low electrical conductivity of reduced graphene oxide may behave as the polarization during charge and discharge process. To achieve the capacity about  $800\text{ mAhg}^{-1}$ , then reduced graphene oxide used in full cell and the electrode should charge about 3.5 V [80].

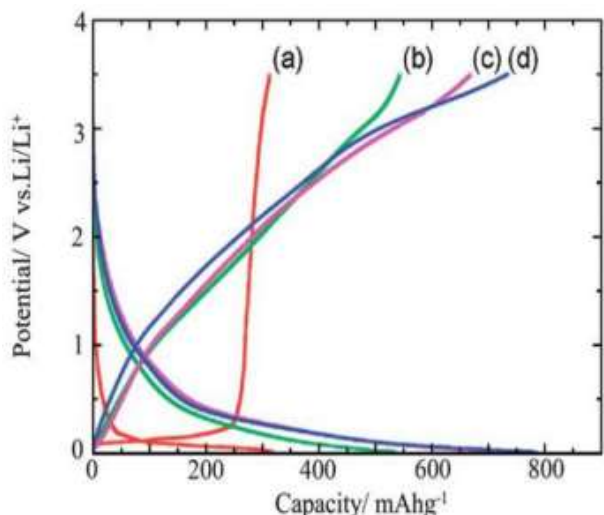


Figure 12 At a current density of  $50\text{ mA g}^{-1}$ , charging and discharging (a) graphite, (b) graphene, (c) graphene with CNT, and (d) graphene with  $\text{C}_{60}$  [88].

With its conductive three-dimensional network, graphene can be utilised to improve the electrical conductivity of composite materials by serving as a structural framework for metal or metal oxide nanoparticle attachment. Transition metal oxides, such as cobalt oxide ( $\text{Co}_3\text{O}_4$ ), ferric oxide ( $\text{Fe}_2\text{O}_3$ ), Tin(IV) oxide ( $\text{SnO}_2$ ), and others, are also viable anode materials. These nanoparticles are either injected or loaded onto reduced graphene oxide during the chemical reduction of graphene oxide [80]. The combination of tin(IV) oxidized and reduced graphene was synthesised by Wang et al. at  $120^\circ\text{C}$  in presence of stannous chloride ( $\text{SnCl}_2$ ) [90] that exhibits 54% cycle efficiency at reversible discharge capacity of  $765 \text{ mAhg}^{-1}$ . Another

anode material that has a high theoretical capacity of  $890 \text{ mAhg}^{-1}$  is cobalt oxide ( $\text{Co}_3\text{O}_4$ ). During the charge/discharge operation, it also suffers from a considerable volume change. Hydrolysis of  $\text{Co}^{2+}$  salt in alkaline media with graphene oxide, followed by calcination of the resultant at  $450^\circ\text{C}$ , can be used to introduce cobalt oxide into graphene sheets. In the first cycle, the  $\text{Co}_3\text{O}_4/\text{rG-O}$  achieves a specific capacity of  $800 \text{ mAhg}^{-1}$ , which reached to  $935 \text{ mAhg}^{-1}$  after passing 30 cycles. In term of capacity of rG-O or simple  $\text{Co}_3\text{O}_4$ , it fell from 955 to  $638 \text{ mAhg}^{-1}$ , or from 817 to  $184 \text{ mAhg}^{-1}$  [91]. Figure 13 exhibits the performance analysis of graphene metal composite.

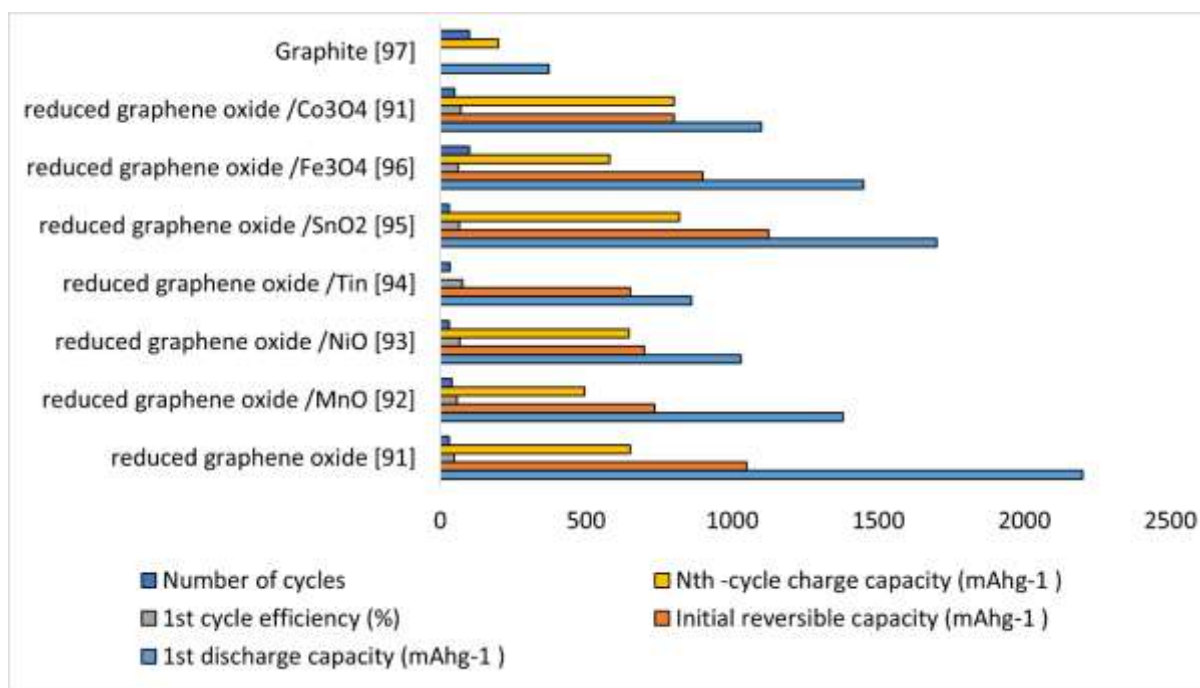


Figure 13: Electrochemical performance analysis of Li-ion anodes using rG-O and graphene metal composite.

### Conclusion and Future scope

The production and anticorrosive properties of graphene and its nanocomposites under corrosive circumstances are summed up in this review paper. In the current collector, the layers of graphene treated as a protective layer against corrosion with the help of chemical inertness, thermal stability. Numerous electrochemical results have demonstrated that, under different circumstances, a thin layer of materials based on graphene significantly reduces the density of corrosion current. Additionally, depending on the experimental procedure, graphene-based composites in the current collector can enhance the graphene nanosheets' anticorrosion qualities by giving the composites better qualities.

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