High-Energy-Density $LiCo_xMn_{2-x}O_4$ Electrodes Decorated with Graphene Oxide and Reduced Graphene Oxide: Electrochemical and Structural Insights

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Abstract:

One of the most significant energy storage technologies that are applied in electronic devices and electric vehicles is Lithium-ion batteries because of the high energy density and the efficient process of charging and discharging. The overall performance of these batteries is mostly based on the characteristics of electrode materials particularly the cathode material which influences the specific capacity, stability of performance, and charge transfer of the battery. $LiCoMnO_4$ (LCMO) is a material of interest in the lithium-ion battery cathodes, as it has the structural and electronic properties that can be utilized in energy storage applications. For examining the impact of temperature on the material's physical properties, LCMO composites were made at three distinct calcination temperatures: 700, 850, and 1000 °C. The findings demonstrated that the preparation temperature affects the composite's surface and electronic properties. For doping with carbon nanomaterials, specifically reduced graphene (rGO) and graphene oxide (GO), in various weight ratios, the sample prepared at 850 °C was used. Electrical conductivity measurement, optical band gap analysis, and specific

surface area analysis with the use of BET (Brunauer–Emmett–Teller theory) were used to examine the physical properties of the prepared composites. Since graphene sheets are 2D, the findings revealed that the addition of graphene improved the electron transport in the composite material as well as augmenting the surface area of the composite. Compared to the pure sample, this resulted in a decrease in band gap values and significant improvement of electrical conductivity. The results indicate that the incorporation of rGO and GO into an LCMO composite may increase the material surface and electronic characteristics, indicating that such nanocomposites may be appealing options in the energy storage processes, particularly in cathode materials in lithium-ion batteries.

Keywords: Li-ion Battery, Cathode, Reduced Graphene Oxide, Graphene Oxide, Electric Vehicles.

Note: The research is based on a PhD dissertation (if any).

Introduction:

Due to the increase in the demand of rechargeable and efficient sources of energy, particularly with the popularity of electric cars, portable electronics, and renewable energy systems, energy storage technologies have evolved rapidly over the past decades. Lithium-ion batteries are also one of the most popular technologies of energy storage as a result of its high discharging and charging efficiency, high energy density, and longer life cycle in comparison with other battery types [1-3].

The overall performance of lithium-ion batteries is largely influenced by the chemical and physical properties of electrode materials, in particular cathode material, which has a direct impact on such characteristics of specific capacity, cyclic stability, and charge transfer rate in the battery [4-6]. One of the most widely used materials in battery cathodes of lithium-ion batteries is transition metal oxides. Such materials have a crystalline structure that can accommodate lithium ions both in the input and output processes during the charge and discharge cycles. $LiCoMnO_4$ (LCMO) is one such material that has been of great interest as a potential energy storage material owing to its structural stability, its capacity to move lithium ions in the crystal lattice, and electronic properties that facilitates charge transfer in the material [7-11]. It

has been shown in many studies that the electronic and structural properties of these materials can be improved to a significant degree that can lead to a substantial improvement in the electrochemical performance of batteries [12-15]. The preparation conditions are important to define physical properties of cathodic compounds. The most crucial of these conditions is the calcification temperature which directly influences the microstructure, the particle size and the regularity of the crystal lattice of the material. Crystallinity and a decrease in structural defects can be achieved by increasing the temperature of preparation to increase the rate of electron transport in the material. Nevertheless, high temperatures may cause agglomeration of particles and decrease in the surface area of a material, potentially affecting the electrochemical performance of the material [16-20]. Conversely, in recent years, there has been considerable attention towards carbon nanomaterials to enhance the electrode materials' workability in lithium-ion batteries. Graphene, GO and rGO are some of the most popular of these materials, which are distinguished by their remarkable physical characteristics, which include large surface area, high electrical conductivity, and high structural flexibility [21-23]. It has been found that by combining these materials with metal oxides it is possible to enhance electron transport and lower the internal resistance of the material, which has beneficial effects on the performance of the battery [24]. A 2D carbon material having a variety of functional groups, including carboxyl, hydroxyl, and epoxide groups, graphene oxide has a strong reactivity with other materials and the capacity to create multifunctional nanocomposites. In contrast, rGO has a better electrical conductivity and a carbon structure that is more similar to pure graphene since a significant amount of the functional groups are removed during the reduction process [25–27]. The properties have contributed to their extensive use in the improvement of surface and electronic properties of electrochemical materials. The sheets of graphene have the potential of being used as electron transport networks between the nanoparticles (NPs) of the active material in cases where carbon materials and metal oxides are mixed to form a composite structure that would provide effective pathways of the transport of electrons in the material. This

enhances electrical conductivity of the composite material and reduces charge transfer resistance [c28-31]. Moreover, the high surface area of graphene can improve the number of active sites for electrochemical processes, making the material more effective in general in batteries. To comprehend the mechanism of charge transfer within such materials, it is critical to examine their surface and electronic properties. An optical band gap is a characteristic that is used to reflect the nature of electron transport in a material; a smaller band gap is used to reflect an easier ability of the material to transfer electrons between conduction band and valence band. Another basic property which defines the transfer of charge through a material during electrochemical processes is electrical conductivity [32]. Moreover, BET technology to study specific surface area is a valuable method of studying the surface properties of nanomaterials, since surface area is associated with the number of active sites in which chemical and electrochemical reactions can occur. Research has indicated that as the surface area of a material is increased, the better a material can be in terms of energy storage application because of enhanced interaction between the material and the electrolyte [33-37]. The connection between the structural, surface, and electronic characteristics of nanomaterials is important in the development of effective cathode materials in lithium-ion batteries. The correlation between surface area (BET), band gap, and electrical conductivity could give a good idea of the charge transfer mechanism within the material. Many studies have demonstrated that adding 2D carbon materials including graphene, GO and rGO to cathode materials can enhance surface area and electrical conductivity by generating effective electron transport pathways, which positively influences the electrochemical characteristics of batteries.

For the purpose of investigating the impact of temperature on the material's physical properties, the $LiCoMnO_4$ (LCMO) compound was prepared in this work at three distinct calcination temperatures: 700, 850, and 1000°C. In order to investigate the impact of such carbon materials on enhancing the compound's electronic and surface properties, the sample that had been

prepared at 850°C was chosen to undergo the doping process with the use of rGO and GO at various weight ratios.

Experimental work

With the use of the same preparation procedures, raw materials, and reaction conditions as detailed in our earlier study [38–39], The cathode material, LiCoMnO4, was prepared using the sol-gel method. The following raw materials were used: Lithium acetate dihydrate (LiCH3COO·2H2O) with a purity of 99% from Fluka, India; Cobalt acetate tetrahydrate (Co(CH3COO)2·4H2O) with a purity of 98% from Fluka, India; and Manganese acetate tetrahydrate (Mn(CH3COO)2·4H2O) with a purity of 99% from Fluka, India. Graphene oxide (GO) and reduced graphene oxide (rGO) were also obtained from the same supplier. In order to examine the impact of temperature on the material's physical properties, the compound was first ground into a powder and after that calcined at three distinct temperatures: 700, 850, and 1000 °C. After that, the samples underwent heat treatment and milling to produce the required phase. The sample prepared at 850 °C was chosen for doping with 2D carbon nanomaterials, GO and rGO, based on initial findings. The nanocomposites were produced at three different weight percentages (1%, 3% and 5%), to study the effects of these carbon materials in the improvement of electronic and physical characteristics of the composite. Various diagnostic tests have been performed to test the properties of the prepared materials. Although the electrical conductivity was determined to investigate the charge transport behavior of the different samples, optical absorption spectroscopy was employed in analyzing optical band gap. The surface area was calculated by using BET spectroscopy to determine the effect of the addition of graphene materials on the surface area and surface properties of the prepared composites. These experiments were conducted to evaluate the effect of adding rGO and GO for improving the physical properties of LCMO composite and to understand the connection between the electronic structure, surface area and the electrical conductivity of the prepared composites.

Results and Discussions

The XRD patterns of the synthesized LCMO at various temperatures, including 700, 850, and 1000 °C. The crystallite size is one of the most important parameters for the characterization of nanostructured materials, which can be estimated by means of the Williamson-Hall relation [44]:

$$D_{hkl} = \left(\frac{K\lambda}{\cos\theta \cdot \beta_{hkl}}\right) + (4\varepsilon \sin\theta) \quad \ldots (1)$$

Where D (nm) is the crystalline size, k is dimensionless shape factor (0.89), λ is the wavelength radiation of the used X-ray (nm), β_{hkl} is the full width at half maximum (FWHM) of the diffraction peaks, and θ (rad) is the radian diffraction angle. All observed reflections have been indexed in the spinel structure according to ICDD 01-070-4214, ICSD 98-020-1557, and ICDD 01-081-1953 cards for $Li_2CoMn_3O_8$, $Li_2Mn_2O_4$, and Li_2MnO_3, respectively, as shown in Fig. 1 and table 1. Both synthesized samples with calcinated at (700 and 850) °C exhibited diffraction lines were attributed to pure LCMO according to peaks of (111), (311), (222), (400), (331), (511), (440), (531), (533), (622), (444), and (551) are crystal planes of the spinel structure $Fd\bar{3}m$. The dominant phase in the calcinated samples related to a peak of (111) at 2θ= 18.93°, and18.74° for that calcinated at (700 and 850) °C, this result in agreement with another researcher [45]. While that calcinated at 850 °C exhibited a vanishing of (533) crystal planes. On the other hand, in the XRD pattern of the sample synthesized at (700 and 850) °C, the peaks assigned to (111) are observed, indicating that the cation distribution in the spinel structure is $Li[Co_xMn_{2-x}]O_4$ in which the Mn ions located at the 16d site are replaced with Co ions. That gives this sample an advantage, especially with the relative increase of the characteristic peaks. As well as with the calcinated with 1000 °C showed other phases, where $Li_2Mn_2O_4$ and Li_2MnO_3 phases were additional appearances with planes of (211) and $(1\bar{1}3)$, respectively. The decrease in the $Li_2CoMn_3O_8$ peaks can be attributed to the possibility that the lithium in the cubic phase is withdrawn by the oxidation of Mn that occurs from/ into the tetrahedral 8a sites occurs at 4 V [46-50].

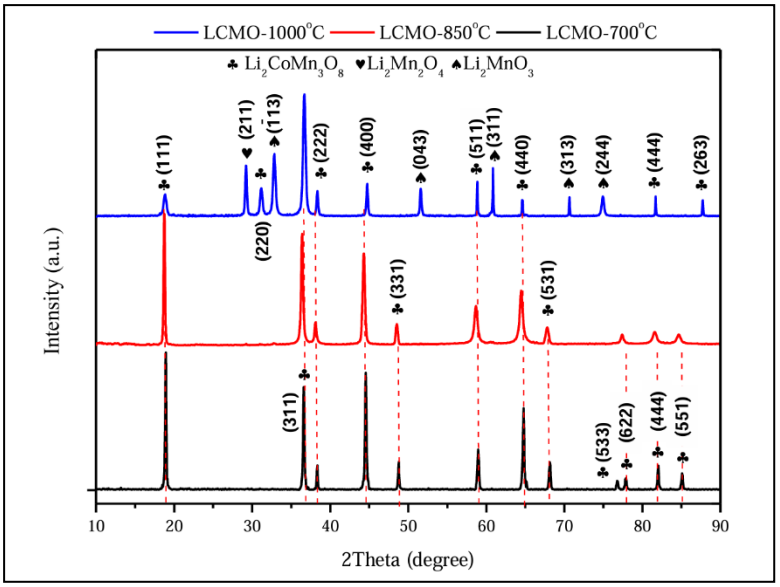


Fig. 2. XRD patterns of the synthesized LCMO at various temperatures of 700°C, 850°C, 1000°C

The XRD patterns of GO (1%, 3% and 5%) and RGO (1%, 3% and 5%) doped $LiCo_{0.5}Mn_{1.5}O_4$ are shown in Figures 2. The all samples show cubic $Li_2Co_1Mn_3O_8$ crystallographic lattice with the $Fd\bar{3}m$ space group. The characteristic diffraction peaks of samples at about 18.9°, 36.7°, 38.4°, 44.5°, 48.8°, 58.9°, 64.7°, 68.1°, 76.7° and 77.8° are in accordance with (111), (113), (333), (321), (044), (222), (333), (044), (335) and (226) planes of cubic $Li_2Co_1Mn_3O_8$ structure with a $Fd\bar{3}m$ space group. Moreover, no peak for grapheme oxide and reduced graphene oxide was noticed in the XRD patterns. According to Figure 2, it can be seen that the intensity of the peaks has not changed much with the increase of doping level of GO and RGO.

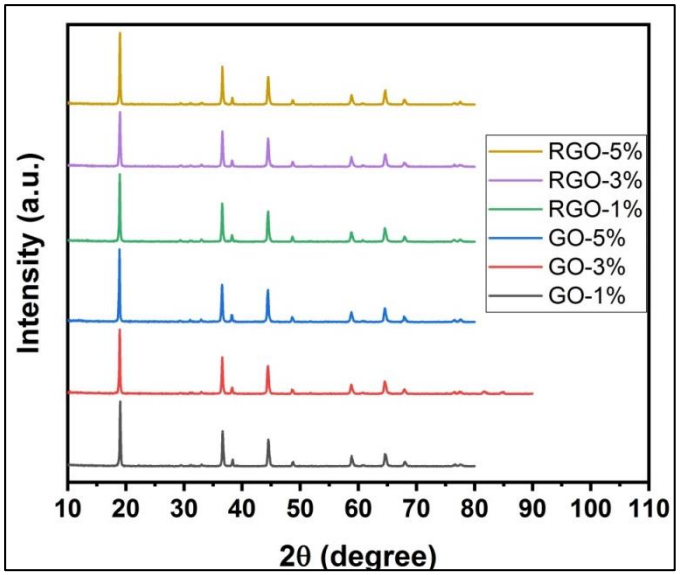


Fig. 2. XRD patterns of the synthesized LCMO (850^{0}C)/GO, RGO at various ratios 1%, 3%, 5% wt

Table 1. Summary of structural parameters obtained from XRD analysis

Sample	2θ (degree)	FWHM	Crystallite size (nm)	Intensity (counts)	hkl	d-spacing (Å)	Lattice constant (Å)
Pure LCMO-700°C	36.65	0.20	53.6	293	311	2.450	8.126
Pure LCMO-850°C	36.46	0.34	65.3	714	311	2.462	8.165
Pure LCMO-1000°C	36.33	0.37	91.8	84	311	2.471	8.195
LCMO/GO 1%	36.64	0.21	41.6	431	311	2.450	8.125
LCMO/GO 3%	36.56	0.21	40.8	417	311	2.456	8.145
LCMO/GO 5%	36.53	0.21	41.0	444	311	2.458	8.152
LCMO/RGO	36.565	0.21	40.8	456	311	2.455	8.142

1%							
LCMO/RGO 3%	36.59	0.23	38.2	407	311	2.454	8.139
LCMO/RGO 5%	36.59	0.19	46.2	438	311	2.454	8.139

According to Table 1, the lattice parameter decreased in the presence of the GO and RGO nanosheets compared to the value obtained for the pure LCMO-900°C sample, due to variations in the actual stoichiometry (partial mixing of the positions of Li, Co, and Mn cations and possible vacancies in the positions of cations and oxygen) [173]. However, the difference in the lattice parameter values for the GO and RGO-containing samples is lower than 0.4% and so is meaningless. Furthermore, the reported results in Table 1 represent that incorporating GO and RGO nanosheets into the composite led to a significant reduction of the crystallite size compared to the value obtained for the pure sample (pure LCMO-850°C). This can be because the GO and RGO nanosheets decrease the crystalline structure's internal residual strain, which can facilitate the grain growth process [174]. In addition, the significant effect of the additives on the crystallite size can verify a full exfoliation of GO and RGO sheets into the nanocomposite.

The Tauc plot approach, which depends on the relation between the absorption coefficient and the photon energy in accordance with equation [37], was used to measure the optical energy gap of the samples.

$$\alpha h\upsilon = A\,(h\upsilon - E_g)^n \quad \ldots. (2)$$

where $h\upsilon$, α and A represent photon energy, absorption coefficient and constant, respectively; n is equal to 2 for indirect transition. The plots of $(\alpha h\upsilon)^2$ vs. $h\upsilon$ are depicted in Fig3 for all of the samples. The bandgap energy (E_g) has been estimated from the intersection of extending the linear part of $(\alpha h\upsilon)^2$ with abscissa axis $h\upsilon$. The obtained band-gap energy values for the samples have been listed in Table2.

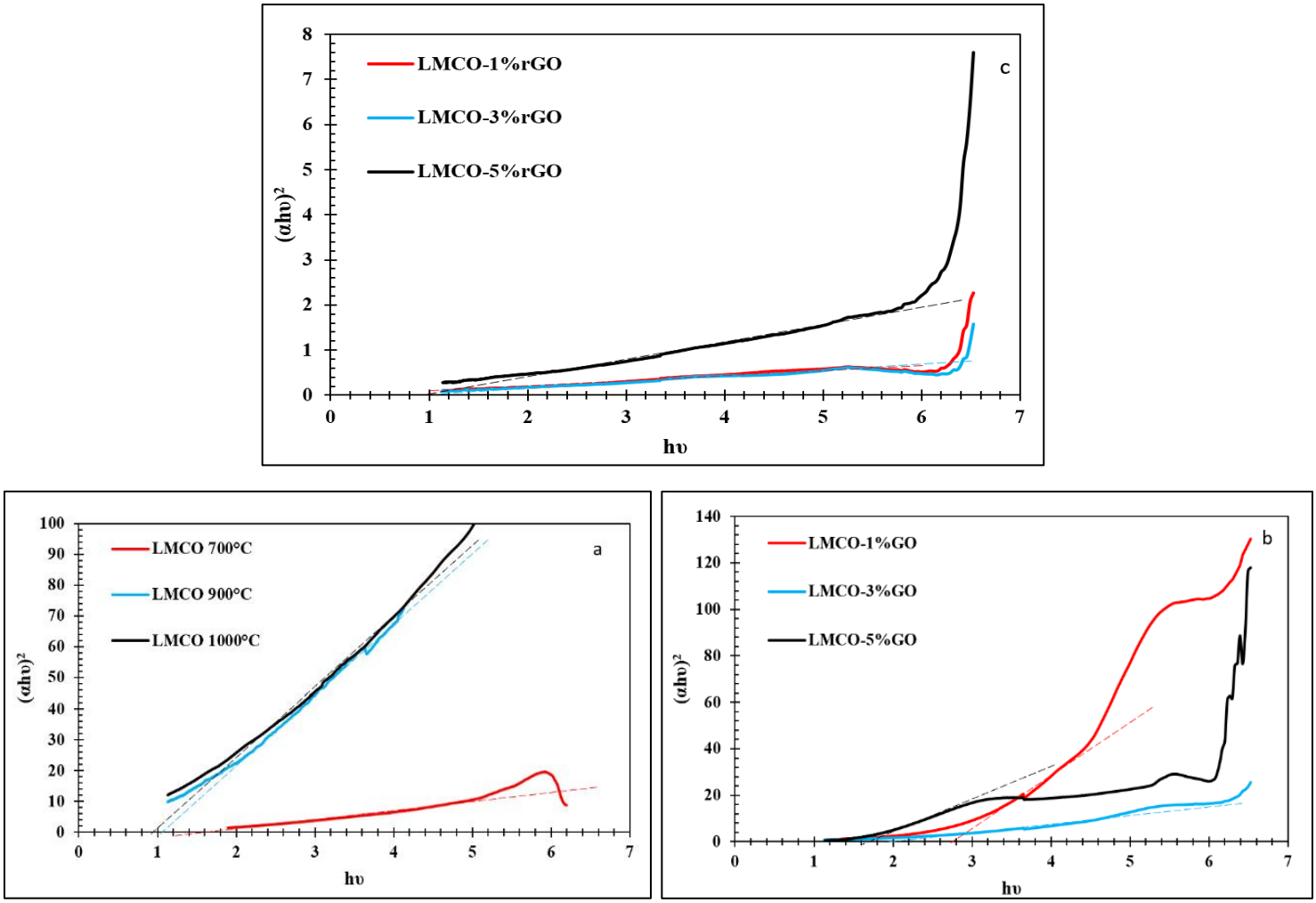


Fig 3. The plots of $(\alpha h\upsilon)^2$ versus hυ for determination of the band gap energy values

Table 2. The band gap energy values obtained from Tauc equation

Sample	Band gap energy (eV)
LMCO 700°C	1.4
LMCO 850°C	1.1
LMCO 1000°C	0.9
LMCO-1%GO	2.8
LMCO-3%GO	2.0
LMCO-5%GO	1.7
LMCO-1%RGO	1.0
LMCO-3%RGO	1.1
LMCO-5%RGO	1.1

The results showed that the energy gap of pure LCMO samples decreases with increasing calcination temperature. This reduction in the energy gap may be attributed to raising the crystallinity, and the increasing regularity of the crystal lattice with temperature which reduces the number of structural defects in the material and, therefore, changes the distribution of the energy levels within the electron bands. The better the crystal structure, the more regular the interatomic distances are and the lower the energy required to transfer electrons to the conduction band is, the higher is the valence band [40]. As the material was mixed with GO, an additional reduction in the energy gap was realized. This is explained by the fact that oxygen-rich functional groups of the GO, which include hydroxyl, carboxyl, and epoxy, are free to react with the surface of the nanomaterial, and form new chemical bonds thereby lowering the effective energy gap value [41]. Nonetheless, in the case of RGO, the energy gap was quite stable as compared to GO-doped samples. This can be attributed to the fact that there are less oxygen functional groups in RGO that decreases chemical interaction with the surface of the material and restricts its action to enhancing the transportation of electrons and not altering the material's electronic structure. The resulting change in the energy gap directly affects the electrical properties of materials because a reduction in the energy gap helps the movement of electrons in the material and causes an increase in electrical conductivity.

The Brunauer–Emmett–Teller (BET) method has been utilized for determining the samples' specific surface area. This method relies on measuring the amount of gas adsorbed onto the material's surface and then calculating the total surface area of nanoparticles [42] as shown in fig. 4.

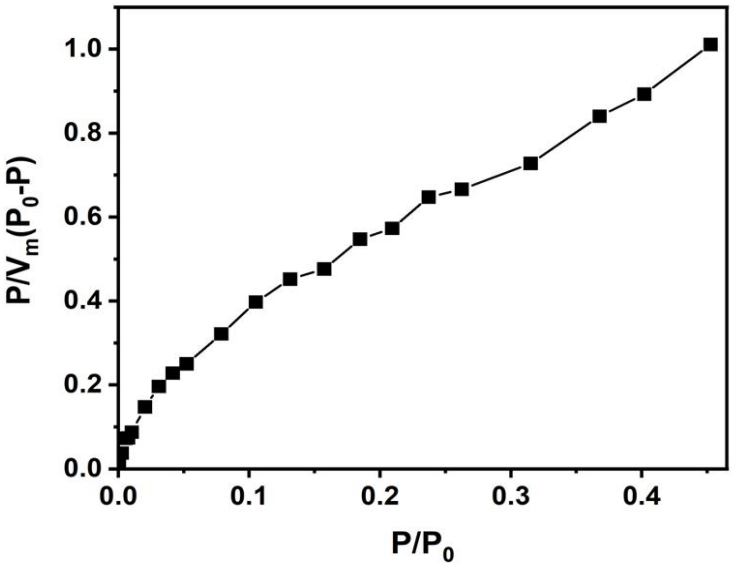


Fig. 1. The BET plot of pure LCMO prepared at 850°C

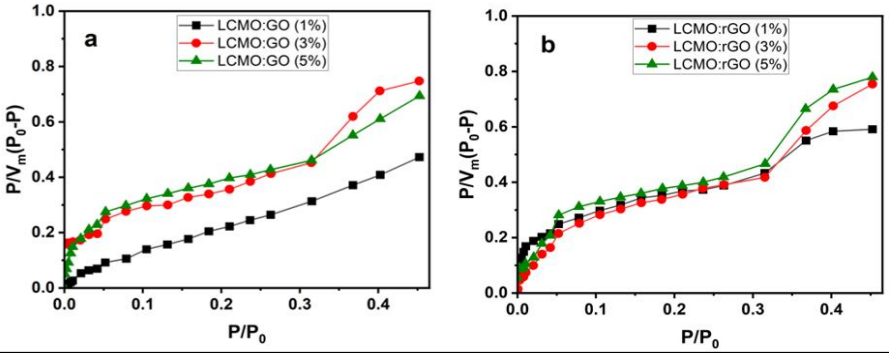


Fig. 4. BET plot of (a) Go doped LCMO and (b) rGo doped LCMO

The findings demonstrated that the pure LCMO sample had a smaller surface area than the graphene-doped samples. This outcome could be indicated by the fact that during the calcination process, the NPs in the pure

sample have a tendency to clump together, which lowers the effective surface area. The material's surface area greatly expanded upon the addition of RGO or GO. This is because graphene materials are 2D and have a large number of effective sites on their surface due to their very large theoretical surface area of about 2630 m^2/g. In addition to preventing NP agglomeration, graphene's lamellar structure produces a more uniform porous structure. Through expanding the area of contact between the electrolyte and the active material, this porosity enhances lithium-ion transport within the electrode [43].

Because of the increased number of lithium storage sites within the material's nanostructure, numerous studies have demonstrated that increasing the surface area of carbon materials utilized in electrodes enhances battery capacity [44]. Additionally, the porous structure that is created by the use of graphene materials aids in lowering the lithium ion diffusion distance within the material, improving the speed at which lithium-ion batteries charge and discharge. Alternating current (AC) and direct current (DC) conductivity measurements were used to examine the samples' electrical properties, as seen in Figs. 5 and 6. The findings demonstrated that all samples' electrical conductivity increase as the temperature increase. Higher temperatures increase the amount of electrons that can move into the conduction band, improving the electrical conductivity, which is a behavior of semiconductors. As indicated in table 3, the results also showed that the addition of graphene significantly increased electrical conductivity when compared to the pure sample. This is because graphene's tremendous electron mobility within its 2D structure makes it one of the best electrical conductors [45]. By acting as a conductive network for electrons, the graphene sheets in the composite material enable charge transfer between NPs and lower the electrode's electrical resistance. Because of the improved electron transport within the material, conductive carbon materials like carbon black or graphene have been shown in numerous experiments to enhance battery performance when added to lithium battery electrodes. Additionally, fast electron transport pathways made possible by graphene's 2D structure increase the rate of electrochemical processes within the

electrode. As a result, graphene-containing composite materials frequently perform better electrochemically than conventional electrode materials.

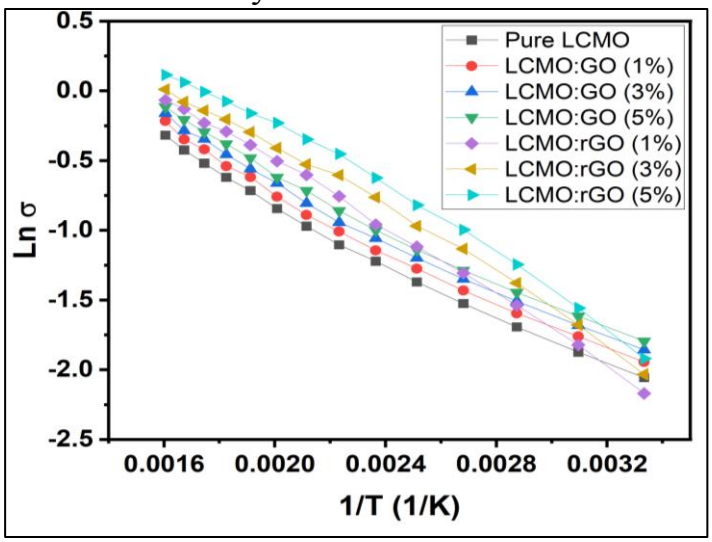


Fig. 5. ln(σ) vs 1/T curves for pure LCMO, LCMO:GO (1%, 3% and 5%) and LCMO:rGO (1%, 3% and 5%)

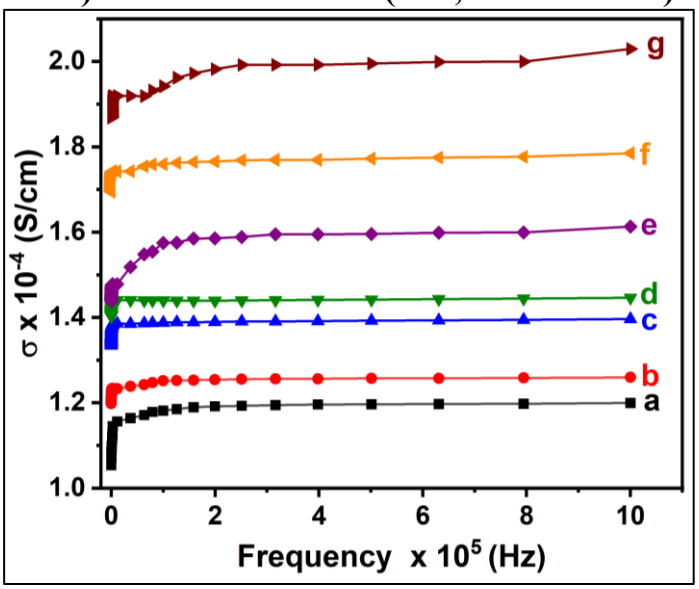


Fig. 6. AC Conductivity vs frequency for (a) pure LCMO, (b) LCMO:GO (1%), (c) LCMO:GO (3%), (d) LCMO:GO (5%), (e) LCMO:rGO (1%), (f) LCMO:rGo (3%) and (g) LCMO:rGO (5%)

Table 3. Activation energy values of pure LCMO, LCMO:GO and LCMO:rGO

Sample	Pure LCMO	LCMO:GO			LCMO:rGO		
		1%	3%	5%	1%	3%	5%
E_a (eV)	0.087	0.086	0.085	0.085	0.104	0.099	0.100

Fig. 8 shows that the relationship between the energy gap (Eg) and the activation energy (Ea) is not directly linear, as the distribution of the dots indicates that the behavior of the samples varies depending on the type of addition. It also shows that the effects of GO and rGO are not identical on the electronic properties, indicating that the transport behavior in this system is influenced by additional factors such as the interface nature and microstructure, and not solely by the energy gap.

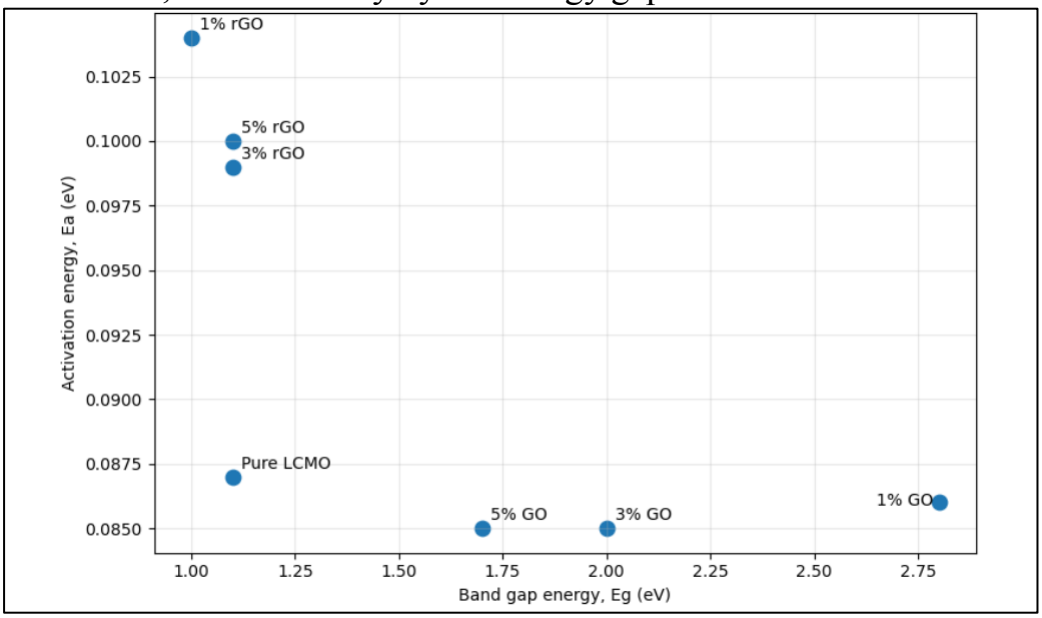


Fig. 8. Relationship between Band Gap Energy and Activation Energy

The discussion of the above findings shows a relation between optical, surface and electrical properties of the materials investigated. Minimal

energy gap enables transport of electrons in the material which results in increased electrical conductivity. The added surface area of the material due to the addition of graphene at the same time offers more active sites on which electrochemical reactions can occur, thereby improving the storage of lithium ions in the material. Increased contact between the electrolyte and the electrode is made possible by graphene's large surface area and porous structure, which lowers internal battery resistance and enhances ion transport. Additionally, the high conductivity of graphene facilitates the formation of a conductive network for electrons within the electrode, improving electron transport and increasing the effectiveness of discharging and charging procedures. Numerous studies have demonstrated that the synergistic characteristics of the electrical conductivity of graphene, high surface area, and porous structure in combination with cathode materials can lead to improving the electrochemical performance of lithium-ion batteries. Therefore, LCMO/rGO/LCMO/GO composites are good candidates to be applied in the advanced energy storage process because the combination of the improvement of the surface area, energy gap, and electrical conductivity lead to the improvement of the electrical and physical characteristics of the material. The scientific novelty of the proposed research is the study of simultaneous effects of the addition of GO and rGO to $LiCoMnO_4$ (LCMO) material that is utilized as a cathode in lithium-ion batteries with a focus on the relationship between the surface of the material, its optical, and electrical properties. Although conductive carbon materials have been used in most studies to enhance cathode materials, most of them have only studied the electrochemical properties. Yet, the physical relation between the specific surface area (BET), optical band gap, and electrical conductivity of the composite material is the main goal of this study. To gain a deeper insight into the mechanisms that enhance rate of electron transport and lithium-ion diffusion in the material, the effects of the varying amount of graphene materials on the physical properties of the material were studied. A combination of such results provides a comprehensive understanding of the impact of electronics properties of the material and its nanostructure on its performance in energy storage. Consequently, the study provides a superior

understanding of the relationship between the physical attributes and structural composition of graphene-doped cathode materials, which would be useful in the design of superior cathode materials to be utilized in the modern lithium-ion batteries.

Conclusions

Three calcination temperatures—700, 850, and 1000 °C—were used to prepare $LiCoMnO_4$ (LCMO) in accordance with the procedure outlined in our earlier research [1] in order to examine the impact of temperature on the material's properties. After preparation at 850 °C, the sample was selected to be doped with rGO and GO at three weight percentages of 1%, 3% and 5%. The electronic properties of the prepared composites were determined by measuring the band gap, and the charge transport behavior in the samples by measuring electrical conductivity. Along with evaluating the impact of adding graphene materials on expanding the surface area and enhancing the surface properties of the composite, BET technology is utilized in order to analyze specific surface area. The purpose of such tests is to determine how the manufactured composites' surface area and electrical and electronic conductivity properties relate to each other. Additionally, to assess how adding rGO and GO can enhance the LCMO composite's physical properties.

References

[1] Chen, X.; Tian, Y. Review of Graphene in Cathode Materials for Lithium-Ion Batteries. *Energy & Fuels* 2021. DOI: 10.1021/acs.energyfuels.0c04191.

[2] Geng, J.; Zhang, S.; Hu, X.; et al. A review of graphene-decorated LiFePO4 cathode materials for lithium-ion batteries. *Ionics* 2022. DOI: 10.1007/s11581-022-04679-0.

[3] Chang, H.-H.; Ho, T.-H.; Su, Y.-S. Graphene-Enhanced Battery Components in Rechargeable Lithium-Ion and Lithium Metal Batteries. *C* 2021, 7(3), 65. DOI: 10.3390/c7030065.

[4] Qi, C.; Wang, J.; Li, S.; et al. Application of Graphene in Lithium-Ion Batteries. *IntechOpen* 2024. DOI: 10.5772/intechopen.114286.

[5] Qu, Q.; et al. Functional Graphene Coatings in Electrochemical Energy Systems. *Molecules* 2025, 30(7), 1436. DOI: 10.3390/molecules30071436.
[6] Sun, Y.; et al. Graphene quantum dots coated LiCoO2 for improved cycling stability and thermal safety at high voltage. *Journal of Electroanalytical Chemistry* 2020, 866, 114109. DOI: 10.1016/j.jelechem.2020.114109.
[7] Zhang, C.; Lou, J.; Li, J.; et al. Graphene coating-modified LiCoO2 films as high-performance cathode material in quasi-solid-state thin-film lithium batteries. *Applied Surface Science* 2024. DOI: 10.1016/j.apsusc.2024.159769.
[8] Shunaev, V. V.; et al. Graphene/LiCoO2 Thin Films as Promising Cathode Materials for Li-Ion Batteries: An Ab Initio Study. 2025.
[9] Jiang, et al. LiV3O8 and Graphene Oxide Nanocomposite as a Cathode in Lithium-Ion Batteries. *ACS Applied Nano Materials* 2023, 6(21). DOI: 10.1021/acsanm.3c04131.
[10] Yang, Q.; et al. Free-Standing Poly(vinyl benzoquinone)/Reduced Graphene Oxide Composite Films as a Cathode for Lithium-Ion Batteries. *ACS Applied Materials & Interfaces* 2024. DOI: 10.1021/acsami.4c09748.
[11] Wang, F.; Wang, W. Reduced Graphene Oxide/LiMgPO4 Double Layer-Coated Li-Rich 0.4Li2MnO3·0.6LiMn1/3Ni1/3Co1/3O2 for High Performance Cathode. *ACS Omega* 2025. DOI: 10.1021/acsomega.5c01281.
[12] Zhang, X.; et al. Graphene/Ta2O5 co-coating to improve the electrochemical performance of cathode material LiNi0.5Co0.2Mn0.3O2 for lithium-ion batteries. 2024. DOI: 10.1002/slct.202304832.
[13] Zhang, Q.; Zhou, Y.; Tong, Y.; et al. Reduced Graphene Oxide Coating LiFePO4 Composite Cathodes for Advanced Lithium-Ion Battery Applications. *International Journal of Molecular Sciences* 2023, 24, 17549. DOI: 10.3390/ijms242417549.
[14] Kumarov, A.; Yerkinbekova, Y.; Zheng, M.; et al. Plasma-assisted reduced graphene oxide-wrapped Ni-rich cathode materials for Li-ion batteries. *Chemical Engineering Journal* 2025, 525, 170156. DOI: 10.1016/j.cej.2025.170156.

[15] Setyawati, R. B.; et al. High power and thermal-stable of graphene modified LiNi0.8Mn0.1Co0.1O2 cathode by simple method for fast charging-enable lithium ion battery. *Results in Engineering* 2023/2024, 21, 101651. DOI: 10.1016/j.rineng.2023.101651.
[16] He, L.; Peng, J.; Liu, X.; et al. The reduced graphene oxide conductive additives with a certain defect concentration enabling rate-capability of lithium-ion batteries. *Electrochimica Acta* 2024, 511, 145353. DOI: 10.1016/j.electacta.2024.145353.
[17] Zhang, G.; Lin, K.; Qin, X.; et al. Electrosprayed Robust Graphene Layer Constructing Ultrastable Electrode Interface for High-Voltage Lithium-Ion Batteries. *ACS Applied Materials & Interfaces* 2020. DOI: 10.1021/acsami.0c06698.
[18] Khalili Azar, M.; Razmjoo Khollari, M. A.; et al. Enhanced Electrochemical Performance and Thermal Stability of ZrO2- and rGO–ZrO2-Coated Li[Ni0.8Co0.1Mn0.1]O2 Cathode Material for Li-Ion Batteries. *ACS Applied Energy Materials* 2021. DOI: 10.1021/acsaem.0c02865.
[19] Razmjoo Khollari, M. A.; et al. Elevated-temperature behaviour of LiNi0.5Co0.2Mn0.3O2 cathode modified with rGO-SiO2 composite coating. *Journal of Alloys and Compounds* 2020.
[20] Graphene Quantum Dot Surface Coating for Improving the Electrochemical Properties of Li-Rich Layered Oxide Cathodes. *Energy & Fuels* 2022. DOI: 10.1021/acs.energyfuels.2c00873.
[21] Langdon, J.; Manthiram, A. A perspective on single-crystal layered oxide cathodes for lithium-ion batteries. *Energy Storage Materials* 2021, 37. DOI: 10.1016/j.ensm.2021.02.003.
[22] Dong, Y.; Li, J.; et al. Oxide Cathodes: Functions, Instabilities, Self Healing, and Degradation Mitigations. *Chemical Reviews* 2023, 123(2), 811–833. DOI: 10.1021/acs.chemrev.2c00251.
[23] Wang, X.; Meng, X. Surface modifications of layered LiNixMnyCozO2 cathodes via atomic and molecular layer deposition. *Rare Metals* 2023. DOI: 10.1007/s12598-022-02243-3.

[24] Sim, S. J.; et al. Use of carbon coating on LiNi0.8Co0.1Mn0.1O2 cathode material to improve electrochemical performance. *Scientific Reports* 2020. DOI: 10.1038/s41598-020-67818-5.
[25] Lizaso, L.; et al. Waterborne LiNi0.5Mn1.5O4 Cathode Formulation for Sustainable and High-Voltage Lithium-Ion Batteries. *Energies* 2023. DOI: 10.3390/en16217327.
[26] Surface Reconstruction of High-Voltage LiNi0.5Mn1.5O4 Cathodes. *ACS Applied Materials & Interfaces* 2024. DOI: 10.1021/acsami.4c10160.
[27] Böhm, K.; et al. Understanding Heat Generation of LNMO Cathodes in Lithium-Ion Batteries. *Batteries* 2025, 11(10), 357.
[28] Piao, J.-Y.; et al. LiNi0.5Mn1.5O4-δ (LNMO) as Co-free cathode for lithium ion batteries via solution-gel synthesis: Particle size and morphology investigation. *Journal of Alloys and Compounds* 2022.
[29] Liang, W.; et al. Investigation the improvement of high voltage spinel LiNi0.5Mn1.5O4 cathode material by anneal process for lithium ion batteries. *Green Energy & Environment* 2021.
[30] Wang, R.; et al. Granularity control enables high stability and elevated-temperature properties of micron-sized single-crystal LiNi0.5Mn1.5O4 cathodes at high voltage. *J. Materiomics* 2021.
[31] Gao, C.; et al. Inhibit the strain accumulation for 5V spinel cathode by mitigating the phase separation during high voltage stage. *Nano Energy* 2024.
[32] Kiziltas-Yavuz, N.; et al. The effect of dual-doping on the electrochemical performance of LiNi0.5Mn1.5O4 and its application in full-cell lithium-ion batteries. *Ceramics International* 2022.
[33] Influence of Ti doping on microstructure and electrochemical performance of LiNi0.5Mn1.5O4 cathode material for lithium-ion batteries. *Materials Today Communications* 2020.
[34] A review: modification strategies of nickel-rich layer structure cathode (Ni ≥ 0.8) materials for lithium ion power batteries. *Journal of Energy Chemistry* 2021.

[35] Regulating the Heat Generation Power of a LiNi0.8Co0.1Mn0.1O2 Cathode Material via Dual Modification. *ACS Applied Energy Materials* 2022. DOI: 10.1021/acsaem.2c00026.
[36] Edge-Protected Ni-Enriched LiNixCoyMnzO2 Cathode Material with Enhanced Interfacial Stability. *ACS Sustainable Chemistry & Engineering* 2023. DOI: 10.1021/acssuschemeng.2c06720.
[37] AlJaber, G.; et al. Reviewing the Role of Graphene in Li-Ion Batteries Using a Computational Approach. *Nanomaterials* 2025, 15(13), 992.
[38] Waleed K. Mahmooda, Asama N. Najea. Study the effect of different temperatures on structural and morphological features of Co-Doped LiMnO4. Chem. Methodol., 2022, 6(12) 985-996
[39] W. K.. Mahmood and A. N.. Naje, "Preparation and Characterization of LiCoMnO4 for Lithium-Ion Battery", *Iraqi Journal of Science*, vol. 63, no. 3, pp. 1039–1044, Mar. 2022, doi: 10.24996/ijs.2022.63.3.13.
[40] Pasero, D., de Souza, S., Reeves, N., West, A. R., "Oxygen content and electrochemical activity of LiCoMnO4–δ". Journal of Materials Chemistry, 15, (2002)
[41] S. Mandal, R. M. Rojas, J. M. Amarilla, P. Calle, N. V. Kosova,V. F. Anufrienko and J. M. Rojo, Chem. Mater., 14, 1598, (2002).
[42] ik Reeves-McLaren, Ma Hong, Hazzaa Alqurashi, Lu Xue, Joanne Sharp, Anthony J.Rennie, Rebecca Boston, "The Spinel LiCoMnO4: 5V Cathode and Conversion Anode", Energy Procedia Volume 151, October, Pages 158-162, (2018)
[43] Anna Windmüller, Chih-Long Tsai, Soren Moller, Matthias Balski, Yoo Jung Sohn, Sven Uhlenbruck, Olivier Guillon, "Enhancing the performance of high-voltage LiCoMnO4 spinel electrodes by fluorination", Journal of Power Sources, Volume 341, 15 February, Pages 122-129, (2017).
[44] Long Chen, Xiulin Fan, Enyuan Hu, Xiao Ji, Ji Chen, Singyuk Hou, Tao Deng, Jing Li, Dong Su, Xiaoqing Yang, Chunsheng Wang, Chem 5, 896–912, April 11, Elsevier Inc, (2019).
[45] Ahmad A. Hasan. Dielectric Study of PVC-LiF Composites Films. Iraqi Journal of Science, 62(3), 861-870, (2021).

أقطاب كهربائية عالية الكثافة الطاقية من $LiCoxMn2-xO_4$ مزينة بأكسيد الجرافين وأكسيد الجرافين المختزل: رؤى كهروكيميائية وبنيوية

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مستخلص البحث:

تُعدّ بطاريات الليثيوم أيون من أهم تقنيات تخزين الطاقة المستخدمة في الأجهزة الإلكترونية والمركبات الكهربائية، وذلك لما تتميز به من كثافة طاقة عالية وكفاءة في الشحن والتفريغ. ويعتمد الأداء العام لهذه البطاريات بشكل أساسي على خصائص مواد الأقطاب الكهربائية، ولا سيما مادة الكاثود التي تؤثر على السعة النوعية، واستقرار الأداء، ونقل الشحنة في البطارية. يُعدّ LiCoMnO4 (LCMO) مادةً واعدةً في كاثودات بطاريات الليثيوم أيون، لما تتمتع به من خصائص بنيوية وإلكترونية تُتيح استخدامها في تطبيقات تخزين الطاقة. ولدراسة تأثير درجة الحرارة على الخصائص الفيزيائية للمادة، تمّ تحضير مركبات LCMO عند ثلاث درجات حرارة تكليس مختلفة: 700 و850 و1000 درجة مئوية. وأظهرت النتائج أن درجة حرارة التحضير تؤثر على خصائص سطح المركب وخصائصه الإلكترونية. ولتطعيم المركب بمواد نانوية كربونية، وتحديدًا الجرافين المُختزل (rGO) وأكسيد الجرافين (GO)، بنسب وزنية مختلفة، استُخدمت العينة المُحضّرة عند 850 درجة مئوية. ولدراسة الخصائص الفيزيائية للمركبات المُحضّرة، استُخدمت قياسات التوصيل الكهربائي، وتحليل فجوة النطاق البصري، وتحليل مساحة السطح النوعية باستخدام نظرية برونـاور-إيميت-تيلر (BET). بما أن صفائح الجرافين ثنائية الأبعاد، فقد كشفت النتائج أن إضافة الجرافين حسّنت نقل الإلكترونات في المادة المركبة، بالإضافة إلى زيادة مساحة سطحها. وبالمقارنة مع العينة النقية، أدى ذلك إلى انخفاض في قيم فجوة النطاق وتحسن ملحوظ في الموصلية الكهربائية. تشير النتائج إلى أن دمج أكسيد الجرافين المختزل (rGO) وأكسيد الجرافين (GO) في مركب LCMO قد يزيد من خصائص سطح المادة وخصائصها الإلكترونية، مما يدل على أن هذه المركبات النانوية قد تكون خيارات واعدة في عمليات تخزين الطاقة، وخاصة في مواد الكاثود في بطاريات الليثيوم أيون.

الكلمات المفتاحية: بطارية ليثيوم أيون، كاثود، أكسيد الجرافين المختزل، أكسيد الجرافين، المركبات الكهربائية.

ملاحظة: يستند هذا البحث إلى أطروحة دكتوراه (إن وجدت).