The effect of adding graphene nanoparticles to the thermal performance of \( \text{LiCo}_{0.525}\text{Ni}_{0.475}\text{O}_2 \) cathode materials in Li-ion batteries

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Abstract. In this work, the effect of adding graphene to the performance of layered \( \text{LiCo}_{0.525}\text{Ni}_{0.475}\text{O}_2 \) (LCNO) cathode materials was investigated. Cathode materials \( \text{LiCo}_{0.525}\text{Ni}_{0.475}\text{O}_2 \) (LCNO) were prepared using a self-propagating combustion reaction. Graphene (G) was added to the prepared compound (LCNO) in different weight percentages to obtain LCNO/G (LCNOG) to improve cathode performance. The powder was divided into four parts weighing 10 g each, and the parts were mixed with percentages weighing 0, 0.5, 2, 4 and 6\% of graphene with 200 ml of ethanol; they were then stirred several times at room temperature to dry completely. The effect of graphene weight percentages on LCNOG mass loss was studied using thermo-gravimetric analysis (TGA). It was concluded that all of the added percentages of graphene behaved the same in all temperatures, except for 6\% added graphene, where it demonstrated inverse behaviour at a high temperature. To determine the optimum annealing temperature range, TGA was identified at 650, 750 and 850 °C for 12 hours in the air. The X-ray diffraction (XRD) patterns of the LCNO and LCNOG showed the crystallisation of all powders in the space group R-3m and hexagonal axes for the crystal system. Energy dispersive spectrometry (EDS), field emission scanning electron microscopy (FE-SEM), a vibrating sample magnetometer (VSM) and atomic force microscopy (AFM) were also used. The LCNOG surface morphology consisted of regular coverage of nano-crystalline grains and random orientation.

Keywords: Lithium-ion batteries, graphene, nanostructures, thermal properties

Introduction

Li-ion batteries (LIBs) are considered the most prevalent energy storage device nowadays; therefore, they are widely used in various areas, such as portable electronics and electric vehicles [1, 2] because comprehensive polarisation occurs with greater current densities [3]. The researchers’ efforts focused on replacing all of the fossil fuels with other renewable energy resources [4]. The LIBs efficiency and energy density is based on the electrode’s physical and chemical properties. In general, the concentration of electrons (or holes) inside semiconductor materials is small, therefore, the interactions of magnetic exchange are super interactions [4–6]. Battery safety is studied in terms of temperature resistance, which is the temperature needed for the thermal runaway process to start. One of the problems of thermal runaway is that the exothermic reactions are chained, which can lead to igniting one after the other [7]. One of the ways to prevent reactions from ending in an explosion or fire is using components with more thermal stability.
Recently, the researchers became interested in graphene for its unique properties, such as its large surface area compared with mass ratio, very high conductivity and high chemical stability. Therefore, they used graphene to develop energy storage sources [8], improve the performance of solar cells, supercapacitors, fuel cells and Li-air batteries [9]; they also used graphene as an additive material to improve the performance of Li-ion batteries [10].

Graphene could be considered an ideal material to create a composite for use in LIB electrodes. Graphene is a sheet material that consists of sp2-hybridised carbon atoms that are organised in a hexagonal crystal lattice 2-D structure, which means that every atom can be estimated as a surface atom [11]. As graphene is a single layer with a thickness of one atom of carbon, lithium ions can be placed between any two layers to make Li2C6, which enables the fabrication of excellent LIB electrodes compared with ordinary carbon electrodes [12].

There are two main methods of graphene fabrication. The first is the top-down method, and the second is the bottom-up method. In the top-down method, graphene sheets are created by disconnecting, or breaking, the graphite stacked in many single layers using the van der Waals forces that connect carbon layers [13]. This method presents some challenges as defects in the graphene sheets’ surfaces and the detached sheets mean that the production method has a low yield [13]. In the second approach (bottom-up), graphene is created using carbon molecules as constructing blocks [14]. However, this method cannot create a graphene sheet with a wide surface area. The most common technique for creating graphene is to make it from graphite using the mechanical cleavage technique, which produces low defect graphene sheets of high quality [15]; nevertheless, this method can be improved. If improved Li-Ion electrodes lead to an increase in the electrode’s ability to store lithium ions, this increases the capacity of the battery. Therefore, researchers believe that batteries with electrodes containing graphene will last longer than conventional batteries [16, 17].

The researchers are focused on energy; as LIBs are one of the few systems with rechargeable energy, they are used widely in different fields [1, 18]. Global energy objectives aim to replace fossil fuels with renewable sources. Therefore, the researchers focused on using alternative and improved cathode materials instead of prepared materials as they have some disadvantages, such as a high cost, high toxicity and weak operating voltage.

The main objective of this work is to improve the performance of the cathode material so that it is less toxic and has a high operating voltage; this was done by adding graphene (G) with different weighted percentages to the LiCo0.523Ni0.477O2 powder.

**Experimental work**

Lithium nitrate (LiNO3), cobalt nitrate (Co(NO3)2·6H2O), nickel nitrate (Ni(NO3)2·6H2O) and citric acid C6H8O7 with 99.99% purity, were bought from Harris Chemicals Corporation in England. The weights were set up at 15.274 g of Co(NO3)2·6H2O, 13.81 g of Ni(NO3)2·6H2O and 6.8942 g of LiNO3.

All of the nitrates were dissolved in deionised water then placed on a magnetic stirring device for 15 min at 25 °C. The mixture was put on a hotplate for 30 min at 100 °C [19–22] then placed in a furnace at 400 °C for 15 min to burn the reaction materials.

A combustion reaction is a chemical reaction affected by factors, such as reaction materials and their impurities; combustion reaction occurs in two steps. The first step is heating the mixture to evaporate the water to make the mixture more viscous [23, 24]. Combustion begins when the water concentrate progressively decreases by evaporation until it reaches a critical point of the threshold temperature value, which is the amount of thermal energy needed to start the combustion reaction process. The second step begins at the moment the reaction is formed (nitric acid and hydroxides), which is due to the dissolution of the nitrate minerals in the water; the intermediate compounds are formed when citric acid is added to the mixture.

Graphene (G) was added to the resulting powder at different ratios of sample weight (0%, 0.5%, 2%, 4% and 6%), and they were labelled S0, S1, S2, S4 and S6, respectively.

Thermal analysis was used to choose the optimum temperature, which led to the removal of impurities that gave rise to phase forms along the crystallisation.
For thermo-gravimetric analysis (TGA), STA-PT1000 from Lenses, Germany was used for powder thermal analysis. The measurement factors were set up with a heating rate of 10 °C/min with the atmospheric pressure staying constant.

X-ray diffraction (XRD-6000) was performed using 2θ, operating at 40 kV and 30 mA X-ray Cu Kα (1.540600 Å) was used to analyse the LCNOG mixture with an FE-SEM. MIRA3 TESCAN was used to investigate the topographies of the LCNOG mixture. To discuss and understand the distribution of particle size, an AFM (Angstrom USA, Spm3000 system) was used. A VSM (Model VSMF 7407) was used to analyse magnetic properties.

**Results and discussion**

Figure 1 shows the curve of TGA pointing to a continuous mass decrease concurrent with temperature increase. Three points located on the plot support the analysis. The percentages of mass loss at the first point (100 °C) were 1.99%, 1.67%, 1.68%, 1.27% and 1.62% for the samples S₀, S₁, S₂, S₃ and S₄, respectively; an endothermic peak was the reason for residual water evaporation from the LCNOG mixture. The second point was located at around 541 °C with an exothermic peak, and all the unreacted materials in the LCNOG mixture combusted at the percentages of mass loss 11.59%, 11.11%, 11.51%, 10.59% and 12.37% for samples S₀, S₁, S₂, S₃ and S₄, respectively. The LCNOG pure phase formed at 700 °C, which represents the third point on the curve, which is in agreement with [25–32]. The mass loss for samples S₀, S₁, S₂, S₃ and S₄ were 16.39%, 14.80%, 14.52%, 13.12% and 16.95%, respectively. Figure 2 shows the comparison between the percentage of mass loss for the samples at temperatures 100 °C, 541 °C and 700 °C.

![Figure 1 Results of the TGA for samples S₀, S₁, S₂, S₃ and S₄](image-url)
Figure 2 The percentage of mass loss for samples $S_0$, $S_1$, $S_2$, $S_3$ and $S_4$ at temperatures 100, 541 and 700 °C.

We noted that at 100 °C, adding graphene caused a reduced mass loss from the LCNOG mixture across all proportions, while in the second and third regions at temperatures of 541 and 700 °C, this behaviour was valid for all additions, except for the 6% addition where it caused an increase in mass loss. This was because the graphene sheets acted as a filler, reinforcing particles that attracted the mixture compound, whereas increasing the mass loss at a high-temperature occurred because the reinforcing effect of graphene reduces the mixture components in segmental mobility. This last enhancement that improved the LCNOG mixture was observed when the graphene ratio increased, and this result was accepted in [23].

At the 850 °C annealing temperature and above, lithium oxide decomposed [10]. When long annealing hours are excluded, a structurally better compound may be formed at high temperatures. Depending on the results of TGA, the temperatures chosen were 650, 750 and 850 °C as the annealing temperatures. This work used EDS analysis to investigate the components that made up the mixture, and the results are revealed in Figure 3. Table 1 shows the weight percentages of Co, Ni, O and C for sample $S_3$ at annealing temperatures of 650, 750 and 850 °C. The results agree with the results in [22, 25–27].

Figure 3 Energy dispersive spectrum of $S_3$ at annealing temperatures 650, 750 and 850 °C.
Table 1 The percentages of powder contents

|                       | Percentage weight at 650 °C | Percentage weight at 750 °C | Percentage weight at 850 °C |
|-----------------------|-----------------------------|-----------------------------|-----------------------------|
| **Carbon (C)**        | 5.30                        | 5.42                        | 4.29                        |
| **Oxygen (O)**        | 29.97                       | 40.03                       | 22.98                       |
| **Cobalt (Co)**       | 35.58                       | 29.19                       | 39.53                       |
| **Nickel (Ni)**       | 29.15                       | 25.35                       | 33.21                       |

There is no peak appearance for Li in Figure 3 because the X-ray of Li K is ultra-soft (about 55 eV), so detecting it is a great challenge; the emitted signal intensity is very weak because the generated X-ray is so small and the absorption probability high [28].

Figure 4 shows the X-ray pattern results before annealing for S0, S1, S2, S3 and S4 powders. The materials have a hexagonal α- NaFeO2 structure with the R-3m space group, which is also the same structure as LiCoO2. The diffraction patterns indicate that all the materials are pure and single-phase, and no impurity peaks were observed.

Figure 4 demonstrates that the predominant phase for LiCo0.525Ni0.475O2 powders is polycrystalline and they are very clear (2θ = 44.823) with Miller indices (105).

The X-ray spectra of LCNOG before annealing show peaks located at around 2θ = 18.841, 37.110, 38.129, 38.767, 44.823, 49.063, 65.781 and 78.647 that was attributed to LiCoO2 (003), (101), LiNiO2 (012), (104), (015) and LiCoO2 (113) and (116), respectively, with an attributed orientation plane. This agrees with the result obtained by Kalyani et al. [29].

Figure 4 X-ray patterns before annealing for S0, S1, S2, S3 and S4 powders

The sharp diffraction peaks in the patterns above indicate the appearance of nano-size crystallite [24, 30–31]. The peak of graphene was detected at 2θ ~ 26.6° corresponding to a d-spacing of 0.335 nm, which is close to graphite d-spacing. Moreover, there was no shift in the diffraction angle positions of LCNO peaks with added graphene, which might refer to the high mobility of graphene.

The XRD patterns for the S0, S1, S2, S3 and S4 samples at annealing temperatures of 650, 750 and 850 °C are shown in Figures 5 a, b and c, respectively.
Figure 5 X-ray patterns for LCNOG with G = 0, 0.5, 2, 4 and 6%; S₀, S₁, S₂, S₃ and S₄ powders at annealing temperatures (a=650 °C, b=750 °C, c=850 °C)

The results of XRD patterns for all the annealing temperatures (640, 750 and 850 °C) show high-intensity peaks that indicate good crystallinity. Furthermore, when the annealing temperature increases, the number of peaks increase. This means that the crystalline size increases when the annealing temperature increases because the annealing process reduces lattice defects and increases retraction. This process can also lead to the adhesion of smaller grains so that the average grain size is larger [32]. The annealing peak of graphene was not seen very clearly. This may be attributed to the low-doped concentration of graphene and the high-intensity peaks of LCNO after annealing. This is a similarity between all peaks and a slight variation in their positions.

The annealing procedure minimises the defects and strains of lattice, but it also causes the coalescence of grains that leads to an increase in the average grain size. The particles of samples are submicron-sized spherical grains, so they can be considered suitable for use in electrochemical applications.

The XRD patterns of LCNOG powders grown by wet-chemistry methods are well-defined with a fine splitting. This refers to a high degree of crystallinity, fine hexagonal ordering and larger characteristics. The XRD results emphasise the composition of the pure phase [33, 34]. However, the characteristics of LCONG powders’ crystalline structures confirmed that the material produced maybe be used as a cathode component with electrochemical properties efficiently compared with others [35, 36].

The 3D topographical structure was tested using AFM for sample S₄ at 650, 750 and 850 °C annealing temperatures, as shown in Figure 6; the area scanned was approximately 3 μm × 3 μm.

The surface roughness of sample S₁ was around 0.24 nm at annealing temperature 640 °C and up to 0.39 nm for 850 ºC. The results showed that the particle sizes were average for sample S₄ at annealing
temperatures of 650, 750 and 850 °C, and were around 71.4, 80.3 and 101.5 nm, respectively. The increase in average particle size and their roughness occurred because of the increase in annealing temperature.

![Figure 6 3D reconstructed images of AFM micrographs of sample S4 at different annealing temperatures](image)

The FE-SEM results showed that when the annealing temperature rises, the interstellar distances between particles decrease and become smaller and more regular; at the same time, the particle size increases, as shown in Figure 7. The results agree with [27]. The electrochemical properties of the material in this work (LCNOG) may be considered promising but may be improved by working to reduce the distances between particles and diffusion.

In our previous study [10], the hysteresis loop measurement of the LCNOG material at annealing temperatures of 650, 750 and 850 °C was studied. The results showed that the LCNOG material had paramagnetic properties and gained a magnetisation factor of 0.8 emu/g in a ±15kOe external field [10].

Both the residual magnetisation (Mr) and saturation magnetisation (Ms) decreased when the particle size increased; however, when the heating and annealing temperature increased, the coercivity force (Hc) decreased.
Figure 7 FE-SEM images of S₃ at different annealing temperatures (a) 650 °C (b) 750 °C (c) 850 °C

Conclusion
This paper presented the thermal properties of LCNO powders after adding graphene at different percentages; this fabricated and characterised the cathode material (LCNO and LCNOG). The addition of graphene to LCNO reduces mass loss because its sheets act as a filler, reinforcing particles that attract the mixture compound. Adding 6% of graphene increased the mass loss at a high temperature because the reinforcing effect of graphene reduces the components’ segmental mobility. The most suitable addition of graphene was at 4%, which had high thermal stability and low mass loss at the annealing temperature of 750 °C.
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