

High Capacity Nanocomposites For Lithium-Ion Battery Anode Material Application

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Abstract: $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) -grapheneplatelets (GPs) and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) -multi-walled carbon nanotube (MWCNT) nanocomposites were synthesized through simple ball-milling followed by sintering process. Scanning electron microscope (SEM) and X-ray diffraction (XRD) were used to characterize the coating structure, particle morphology, and phase structure. SEM micrographs, XRD analysis, showed that both LTO particles achieved highly developed spinel nanocrystal structures averaging between 50nm and 80nm. Electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), and galvanostatic charge/discharge analysis were used to test electrochemical lithium extraction/insertion performance. Both LTO-GPs and LTO-MWCNT nanocomposites showed superior discharge that was above 150mAh g^{-1} at 1C, 5C and 10C rates for 200 cycles. The LTO-GPs nanoparticles had larger enhanced electrochemical Li^+ insertion/extraction kinetics (202mAh/g) at various cycling rates. Comparative electrochemical analysis and structure of two nanocomposites show two outcomes. One, both MWCNT and GPs interconnection networks and nanoscale graphitic covering layers improve lithium kinetic rates. Two, MWCNT and graphene increase electronic conductivity of lithium insertion/extraction in the LTO-GPs and LTO-MWCNT particles.

Key words: Lithium ion battery, Lithium titanium oxide, Multiwalled carbon nanotubes (MWCNT), Graphene platelets (GPs)

1. Introduction:

Most consumer electronics are increasingly being fitted with lithium-ion batteries as the primary power source [1, 2]. In the last few decades, developments of Li^+ batteries have been triggered by increased concerns about environmental pollution and greenhouse gas emissions [3].

However, cycling stability and safety issues have become the critical areas of concern in

the design of better batteries that can deliver large amount of power and possess high energy density [4, 5, and 6]. Among the materials researched for potential anode applications, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) is the most promising material [7, 8, and 9].

For the lithium-ion battery, LTO has become an excellent material for insertion/extraction because of negligible change in volume during the charge and discharge processes [2]. As such, the cycle performance of LTO is reliable making it a suitable anode material [10, 11]. However the lithium insertion plateau of LTO is 1.55V versus Li/Li^+ that are important in preventing decomposition of electrolyte and deposition of metallic lithium [12]. As a result, the degree of security that Li^+ batteries possess is anticipated to increase significantly. Nonetheless, the shielding feature of LTO present in empty Titanium 3d orbital largely contributes to poor capability rates, meaning that such a limitation prevents LTO from large commercial applications [13].

To overcome the above LTO limitations, a number of interventions have been used to improve its electrical conductivity. One of the key interventions includes reducing the size of LTO particles using innovative synthesis procedures to decrease the Li^+ circulation path [14, 15, and 16]. Alternatively, the surface of LTO should be coated with conductive materials [16]. The problem with this approach is that nanoparticles have the capability to attract one another, a move that contributes to increased interparticle contact repulsion [17]. In return, the interparticle resistance limits electrical conduction pathway to the current collecting anode [17, 18].

Moreover, there is another challenge when coating LTO particles over the carbon paper; it is difficult to achieve a uniform surface lining. Hence, achieving a hybrid nanocomposite material as an anode, with a conductive additive anaphase, where it is possible to control particle growth, presents a better material that ensures rapid ionic and electronic transportation [1, 3, 20]. These features are needed to achieve reliable conduction

capability. The solid-state process of ball milling and high-temperature heat treatment is necessary for the preparation of well crystallized and pure LTO powder. However, in solid-state reactions, the fabrication of nanocomposite LTO using high dispersity is often difficult and the same is also true if the sol-gel process is used [5, 21, 19].

Over the decades, MWCNT has been applied as anode material for Li^+ batteries owing to its unique properties like unique conductivity, flexibility, strength, and diameter ratio [20]. Also, graphene has an extraordinary flexible structure, high surface area and mechanical strength for interfacial contact, and better electronic transport properties [23, 25]. Thus, graphene platelets (GPs) and MWCNT are regarded ideal conductive additives to nanostructured hybrid electrodes of lithium-ion batteries [21, 23]. Another important thing of graphene is, it produces chemical reactions when reduced from graphene oxide exposing functional groups like $-\text{OH}$ and $-\text{COOH}$ which provide suitable connections with LTO to form homogenous composite during preparations [24]. However graphene not only increases electrical conductivity it's also improves cyclic stability and capacity of anode materials [20].

The present research provides an efficient and practical solid state process for synthesizing LTO-MWCNT and LTO-GPs nanocomposite materials for lithium-ion batteries. The MWCNT serves as a support matrix with the conductive network, and also serves to prevent aggregation of LTO nanomaterial during calcination. The solid state ball-milling process retains the particle size of LTO to less than 100nm. The LTO-GPs having a suitable entanglement structure which also combine the advantages of both conductive adhesion and nanosized materials to enhance LTO's electrochemical conduction in Li^+ batteries. The LTO-MWCNT and LTO-GPs allows for good cycle performance and also gives superior lithium insertion/extraction performance capacity.

2. Experiment

In order to improve the specific capacity of Lithium titanium oxide (LTO), nanocomposite route was adopted. LTO was incorporated with MWCNT and graphene platelets (GPs) separately in a (70:30) weight ratio. LTO-MWCNT (70:30) and LTO-GPs (70:30) by weight ratio was prepared. Ultra sonication followed by ball milling was used to mix these two mixtures separately for 5 hours under 200 rpm rotational speed in an isopropyl alcohol medium. The slurry product formed was dried at 100°C then sintered in the tubular furnace for 4 hours at 900°C . To compare the products, pure LTO without graphene platelets

and MWCNT were also made. All the raw materials used for these experiments are obtained from Sigma-Aldrich.

In the fabrication of coin cells, the electrodes were prepared on the Toray carbon paper of 15-20-micron thickness. The carbon paper first made hydrophobized using Teflon solution. This makes carbon paper inert towards its reactivity with hydro molecules. Lithium active material (nanocomposites) with conducting carbon (Vulcan XC-72) was well mixed with ball milling added to binder (10% Teflon solution) and made slurry coated on the carbon paper. The electrodes were dried at room temperature. Electrodes of 1.76 cm^2 were cut from the bigger electrodes and then dried in the oven for 48 hours at 85°C . The electrochemical measurement was achieved using (CR-2032) type coin cells with Lithium metal as the reference electrode.

3. Results and discussion

XRD patterns of the prepared nanocomposite materials are elaborated in Figure 1. As evident from the XRD pattern, there are no impurities in LTO and also MWCNTs around LTO nanomaterial's probably as a result of very low amorphous carbon content. The LTO-GPs sample shows diffraction peaks that are consistent with LTO's cubic spinel shape. Any broad lines or peaks that correspond with crystalline or amorphous carbon are of insufficient intensity that could have been detected in the background of XRD pattern of LTO-GPs nanocomposites. No impurities can be observed showing that adding GPs does not have any impact on LTO's crystal structure.

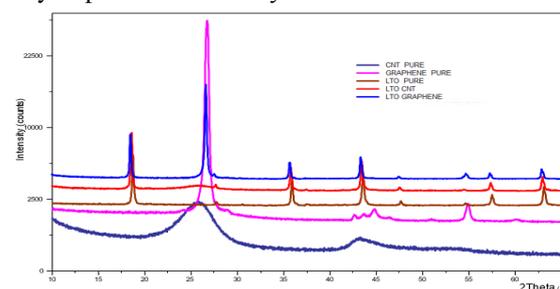


Figure 1: XRD patterns of MWCNT pure, graphene pure, LTO pure, LTO-MWCNTs and LTO-GPs materials.

The diffraction peaks in LTO-MWCNT composite are broad, and their relative peak intensity is less compared to pure LTO. The observed difference is as a result of small sizes of LTO-MWCNTs composite particles. The lattice

parameters of LTO-MWCNTs composite and pristine LTO have been calculated to be 8.37A° and 8.35A° , respectively [3]. In some cases, Ti^{4+} ions transform into Ti^{3+} ions, where some lattice parameters of LTO-MWCNTs composites are anticipated to be larger than 0.67A° compared to Ti^{4+} ions which are 0.61A° . As such, the introduction of Ti^{3+} ions intrinsically increases LTO's electrical conduction [3, 19].

As shown in figure 2b, particles are aggregated to form micro-sized nanomaterial. There are a small number of LTO molecules in the SEM image, emphasizing that few LTO particles were dispersed into MWCNT's electrode surface.

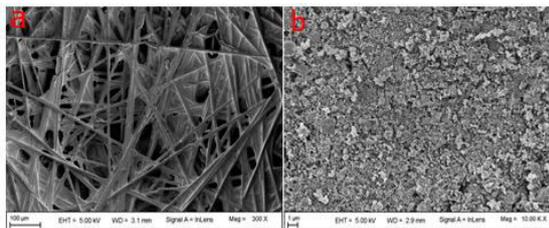


Figure 2: (a) SEM picture of the uncoated electrode, (b) SEM image of coated electrode.

The scattered images reveal several bright spots and areas dispersed on the MWCNTs matrix (Figure 2b). The bright spots and areas show the presence of LTO nanoparticles. The nanoparticles in LTO-MWCNT range between 50nm and 150nm in diameter, and such ranges prevent LTO nanoparticles from aggregating. The entanglement with LTO particles effectively serves to enhance the conductivity of LTO and also the contact in-between individual LTO particles [9].

Figure 3 shows SEM images of LTO-MWCNTs and LTO-GPs nanocomposites. The LTO-MWCNT & LTO-GPs particles are nearly 100-150 nm in size after ball milling, as shown in figure 3a and 3b with some being aggregated. From the SEM image of LTO-GPs, it is clear that the particles were well dispersed between the graphene nanoparticles.

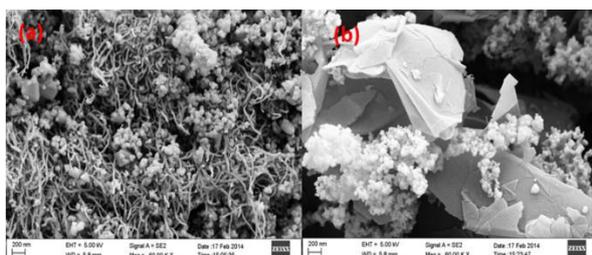


Figure3 : SEM image showing formed nanocomposites; (a) LTO/MWCNT nanocomposite and (b) LTO-GPs nanocomposite.

The graphene also extended across all directions similar to a well stretched network and this gives better conductive connections between the insulating nanoparticles. The connection between graphene and LTO nanosheets (Figure 3b) is clear in the SEM image with well-structured crystals in line with lattice spacing. As such, there is additional evidence of phase purity as graphene particle firmly linking with LTO nanoparticles and preventing them from aggregating further. Moreover, the addition of MWCNT improves LTO connection and prevents LTO particles from aggregating during sintering.

Figure 4 shows results for LTO-GPs, LTO-MWCNT, and pristine LTO. The analysis was undertaken after the cell was charged and discharged after 1 cycle. The measurement was taken after a stable 1.5V voltage. The inclusion of AC impedance spectrum elaborates that the corresponding circuit where (Rct) is the charge transfer impedance, which relates to the resistance of the electrode. The LTO-GPs and LTO-MWCNT shows $15\ \Omega$, $19\ \Omega$, they are lower than the $23\ \Omega$ of pristine LTO. The improved results can be explained as a result of interspace MWCNT entanglement which effectively separates and stops the accumulation of LTO nanomaterials during thermal treatment [7]. The intervention results in small-sized LTO particles that have improved interaction between MWCNT and LTO particles, hence facilitates the transfer of electrons.

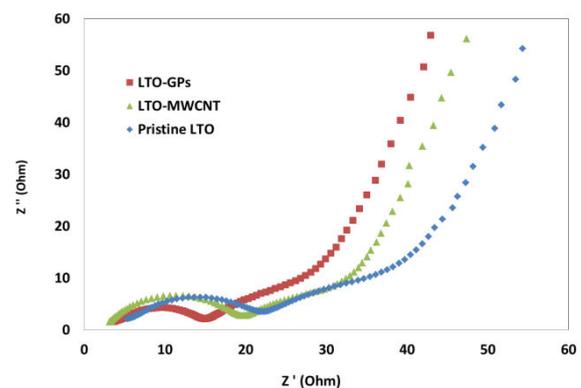


Figure 4: An AC impedance spectra of pure LTO, LTO-MWCNT, and LTO-GPs.

The electrical impedance results in Figure 4 emphasizes that in situ carbon coats can be applied in significant synthesis and enhancing

conductivity of LTO-GPs and LTO-MWCNT. Because graphene and MWCNT facilitates better conductive paths in the lithium-ion battery, the findings prove that these nanocomposites can improve the cycle life, rate capability, and discharge capacity of the batteries.

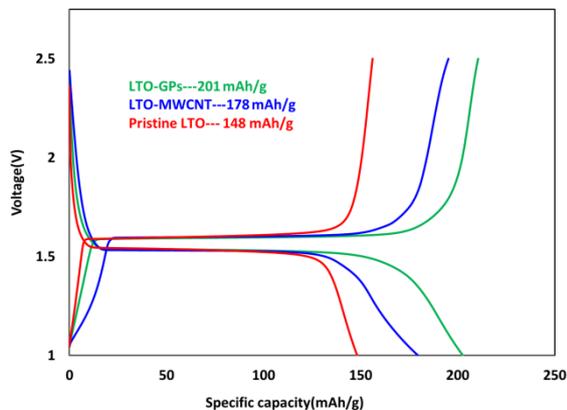


Figure 5: Results showing curves for charge/discharge for LTO, LTO-MWCNT, and LTO-GPs.

Figure 5 shows Galvanostatic charge-discharge was carried at 1C current rate. Specific capacities obtained from 2nd discharge cycle of Pristine LTO are 147mAh/g, LTO-MWCNT is 177mAh/g and LTO-GPs are 202mAh/g respectively.

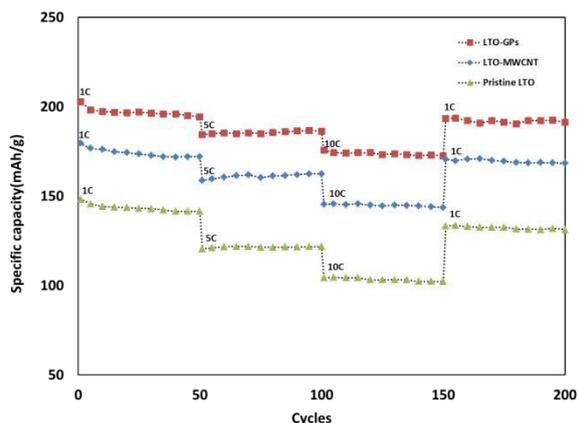


Figure 6: LTO-GPs, LTO-MWCNT and Pristine LTO fifth charge/discharge curves

Figure 6 shows the fifth charge/discharge of LTO, LTO-MWCNT, and as well as LTO-GPs composites electrode at the different current condition, namely 1C, 5C and 10C. Pure LTO shows a loss in capacity by 26% and 15% when the

current is raised from 1C to 10C and 1C and 5C, in that order. This large loss of capacity is as a result of large LTO particle sizes that work to induce poor electrical conduction and longer Li⁺ diffusion [1]. However, the LTO-GPs and LTO-MWCNT show a capacity loss of 10% and 13% when the current is increased from 1C to 10C and capacity loss of 5% and 7% when current is raised from 1C to 5C, respectively. The improved rate of performance is as a result of small particle sizes of LTO, excellent conductive network, and better conductive nanocomposite networks

Figure 7 shows the performance of electrochemical lithium insertion/extraction of LTO-MWCNT, LTO-GPs and Pristine LTO electrodes after characterization by cyclic voltammetry. This was achieved by using 1M LiPF₆ in EC+DMC (1:1) as the electrolyte. The potential was performed in a potential window of 0.8V and 2.5V versus Li/Li⁺. Cyclic Voltammetry of LTO, LTO-MWCNT and LTO-GPs was performed at 2.5 mV/s scan rate. The reversible redox peaks are clearly evidence that the cathodic and anodic peaks for LTO-GPs, LTO-MWCNT composites showing a fast electrode kinetic progression than Pristine LTO.

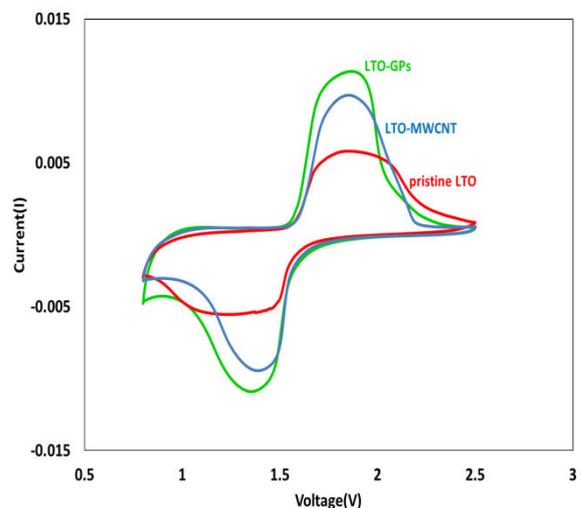


Figure 7: Cyclic voltammetry of LTO-GPs, LTO-MWCNT and Pristine LTO versus Li metal.

4. Conclusion

LTO-GPs and LTO-MWCNT nanocomposites were synthesized using simple ball milling

followed by sintering process. The findings show that the composites have an interspace that appropriately acts as a separator to prevent aggregation of LTO nanomaterials during calcination. The finding further shows that closely connected conductive networks and short lithium ion diffusion pathway improve electrical conductivity. After 200 cycles again at 1C current rate, the discharge volume was above 175 mAh g⁻¹ which indicates a 95% of the previous discharge capacity, Figure 6. As such, the current nanocomposites are reliable materials that can be used in Li⁺ batteries. The current Li⁺ battery will possess a longer cycle life and deliver high power for various appliances.

5. References

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