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Review of Electrode Materials on Lithium Ion Battery

J. P. Harikrishna[1], J. John Sebastain[2], S. Navin[3], P. Chandra Mohan[4]
[1,2,3]*Student, Department of Mechanical Engineering, Sri Ramakrishna Engineering College, Coimbatore, India*
[4]*Professor, Department of Mechanical Engineering, Sri Ramakrishna Engineering College, Coimbatore, India*

***Abstract*: The great demand for high-power lithium-ion batteries has made an extensive research on carbonaceous electrode materials. Herein, we reviewed and reported a facile way of preparing novel carbon nanotubes, with lithium titan ate and graphene. Various electrode materials were studied on their characterization and electrical properties. More over the carbon based materials provide better results. The synergistic effect of graphene and carbon nanotubes constructing 3D networks could enhance the electronic conductivity of Li4Ti5O12/carbon nanotubes/graphene composite.**

***Keywords*: Electronic conductivity, Lithium ions, Electric vechicles.**

1. Introduction

Lithium-ion battery or Li-ion battery (abbreviated as LIB) is a type of rechargeable battery in which lithium ions move from the negative electrode to the positive electrode during discharge and back when charging. Li-ion batteries use an intercalated lithium compound as one electrode material, compared to the metallic lithium used in a non-rechargeable lithium battery. The electrolyte, which allows for ionic movement, and the two electrodes are the constituent components of a lithium-ion battery cell in recent years, rechargeable lithium- ion batteries (LIBs) have been considered as a promising power system for energy storage. Lithium ion batteries are rapidly replacing conventional lead-acid batteries in our daily life from personal portable equipment to large-scale electric energy storage applications such as electric vehicles (EVs) and hybrid electric vehicles (HEVs). Lithium (Li)-ion batteries have been widely used as power sources for portable electronic devices and are emerging into transportation and grid applications, but the energy density of the state-of-the-art Li ion batteries will reach its theoretical limit soon, and new battery designs are urgently needed to satisfy the increasing demand for high-energy-density batteries. In this regard, Li metal anode material has attracted worldwide attention because of its many merits. Although practical applications of Li metal anodes are still limited by several challenges, such as dendrite growth and low columbic efficiency, rapid development of new materials and electrode designs in recent years has overcome many bottlenecks in this field and hastened the practical applications of high energy- density and high performance rechargeable Li metal batteries. In this Perspective, recent significant progress on stabilization of Li metal anodes for Li metal batteries is highlighted. We also present a perspective on future directions and possibilities to better address the existing challenges of Li metal anodes and Li metal batteries.

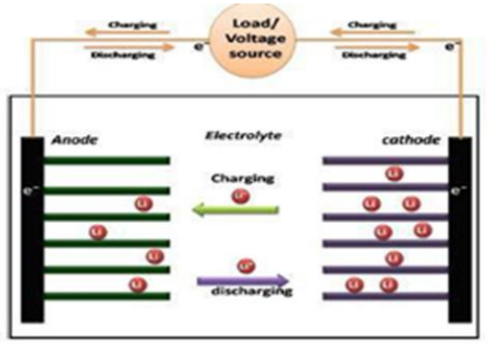

Fig. 1. Working principle of a typical Li-ion cell 2.

2. Literature survey

A. Cathode materials

- Glassy analogs of two important cathode materials for Li-ion cells: $V_2O_5$and phosphoolivine $LiFePO_4$ were heat-treated in order to prepare Nano crystallized materials with high electronic conductivity of up to 7 × 10^{-2}S $cm^{-1}$and ca 7 × 10^{-3}S cm^{-1}at 25∘C. The heat-treatment of the initially glassy samples of two different systems V_2O_5–P_2O_5 and Li_2O–FeO– V_2O_5–P_2O_5 leads to a substantial and irreversible increase in their electrical conductivity accompanied by microstructural changes. In the case of glasses of the Li_2O–FeO–V_2O_5– P_2O_5 system, which were prepared under different conditions from different reagents, one observes similar effects: a conductivity [1].
- Carbon-coating (use of citric acid as a carbon source (5 wt %)) precursors is used to modify the surface of commercial graphite for Li-ion battery anodes. The coating procedure and final carbon content are tuned to study the influence of the precursors on the electrochemical performance of graphite. The coating reduces the first cycle efficiency by 3%–10% compared to pristine graphite due to the increase of the Surface area available for the continuous electrolyte

decomposition and results in the specific capacity at 3^{o}C of 228 mAh g $^{-1}$ vs. 211 mAh g $^{-1}$ for the uncoated graphite [2].

- The conventional carbon coating procedures, chemical carbonization processes, are especially difficult to apply for oxide cathode, which could deteriorate the oxide structure. Here a new dry 100-nm-thick homogeneous multi-walled carbon nanotube (MWCNT) coating is prepared on the high-capacity oxide cathode material, $Li_1.17NiO.17CoO.1MnO.56O_2$, by applying shear stress without breakdown of crystal structure and morphology of the cathode. The electronic conductivity of carbon composite with the coated sample is 170 mS cm^{-1} which is over 40 times as much as the value of the pristine cathode with the same amount of carbon. In addition, at high current condition of 2450 mA g^{-1}, 103 mAh g^{-1} of specific capacity is obtained even with only 3 percent of carbon in weight including the coated MWCNT [3].

B. *Anode materials*

- Carbon nanotubes are promising candidates for use as anode material in lithium ion batteries. As an allotrope of graphite, carbon nanotubes have already been presented as a competitive lithium storage material. Due to their unique structure (one-dimensional cylindrical tubule of graphite sheet), high conductivity (106Sm^{-1} at 300K for single walled CNTs (SWCNTs) and >105Sm^{-1} for multi-walled nanotubes (MWCNTs)), low density, high rigidity (Young's modulus of the order of 1 TPa), and high tensile strength (up to 60 GPa). SWCNTs can have reversible capacities anywhere from 300 to 600mAhg^{-1} this means it can be significantly higher than the capacity of graphite (320mAhg^{-1}), a widely used battery electrode material [4].
- Polycrystalline Ge on vertically aligned multiwall carbon nanotube (MWCNT) arrays (MWCNT/c-Ge) and amorphous Ge on the arrays (MWCNT/a-Ge) were fabricated using a low pressure chemical vapor deposition system and a radio frequency sputtering system, respectively. The vertically-aligned MWCNT arrays were used as a platform to minimize pulverization problem. The MWCNT/a-Ge had a specific capacity of 1096.1 mAhg^{-1} at the rate of 162.4 mAhg^{-1} at the 100th cycle. In comparison, the MWCNT/c-Ge only showed a specific capacity of730.2 mA hg^{-1} at the rate of 162.4 mA g^{-1} at the 100th cycle. The MWCNT/a-Ge sample showed better performances as the MWCNT/a-Ge skipped the electrochemically-driven solid-state amorphization of crystalline Ge during the first lithiation [5].
- Silicon hollow nanostructure ty. The fabricated hybrid structures, carbon-coated silicon nanotube arrays on carbon cloth substrate, with a high surface area and short electron collection pathway have been directly used as anode electrodes without any additional binder. The electrodes exhibit high capacity, excellent rate capability and good cycling stability. The discharge capacity of the hybrid electrode (the deposition time of silicon shell: 5 min) keeps stable, and after 100 cycles, the discharge capacities still remain 3654 mAh g^{-1} at the rate of 0.5oC [6].
- The fabrication of porous carbon nanotubes webs with high level of boron (15.05 at.%) and nitrogen (6.71 at.%) co-doping (denote as BN-PCNTs) by using polypyrrole (PPy) nanotubes as the precursor. Instead of using virulent boron hydride, ammonia borane (NH_3BH_3, denote as AB), a versatile and non-toxic agent, was employed as an effective heteroatoms sources to induce B and N co-doping in mild conditions. Benefiting from the porous nanotube structure and high-level B, N co-doping, the BNPCNTs exhibit high reversible capacity (900 mAhg^{-1} at a current density of 200 mAhg^{-1}) with good cycling and rate performances as anode materials in lithium ion batteries [7].

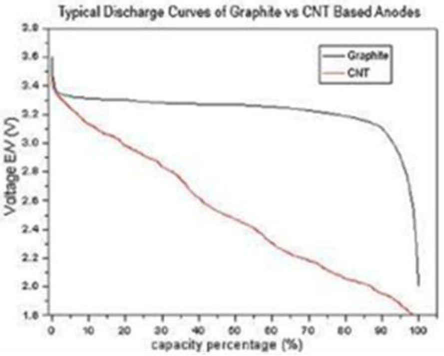

Fig. 2. Discharge curves of a graphite and CNT based anode

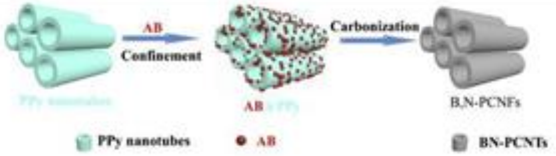

Fig. 3. Preparation of BN-PCNTs

- Carbon nanotubes with high nitrogen doping are used as the anode for li-ion battery. Helical and straight 3-aminophenol formaldehyde resin nanotubes were first prepared based on the self-assembly of the chiral amphiphiles, which were then used as carbon sources to fabricate self-nitrogen-doped carbon nanotubes via pyrolysis process. When the resins were carbonized the anode for li-ion battery. Helical and straight 3-aminophenol formaldehyde resin nanotubes were first prepared based on the self-assembly of the chiral amphiphiles, which were then used as carbon sources to fabricate self-nitrogen-doped carbon nanotubes via pyrolysis process. When the resins were carbonized at

600C, carbon nanotubes with a high nitrogen-content of 9.6 wt% were obtained, which maintained the original morphology of the resins. The electrochemical tests disclosed that the carbon nanotubes exhibited excellent Li storage capacity and superior cycling stability. A high reversible specific capacity of 1056 mAh g-1 at 0.1Ag-1 was obtained after 300 cycles, which is greatly higher than that of graphite and most of polymer derived carbonaceous materials. The research data implied that the nitrogen doping content plays an important role in the electrochemical performance of the carbon nanotubes [8].

- Li_2Na2Ti6O14 was developed from Li5Ti4O12 as a good active material for anode of the lithium battery. Li2Na2Ti6O14 was prepared by a preliminary formation of Li2Na2Ti6O14 through solid state reaction with calcination temperature at 700 oC, and sintering temperature at 800 oC for 8 hours. By analysis of XRD patterns, Li2Na2Ti6O14 shows spinel structure which similar as Li5Ti4O12. Carbon coating on Li2Na2Ti6O14 was done by using pyrolysis method at a temperature of 700 oC for 2 hours. The process of carbon coating was done under variation of comparison between Li2Na2Ti6O14 and tapioca powder as a carbon source, i.e. 8:1, 10:1 and 12:1. The working voltage of Li2Na2Ti6O14/^{o}C product was 1, 2 volt. The other analysis were conductivity, cyclic voltammeter, and charge – discharge [9].
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  Na2Li2Ti6O14/C composite was successfully done with 96% purity obtained from crystal structure analysis. The working voltage of Na2Li2Ti6O14/C was around 1.29 V. The coated carbon on anode material of Na2Li2Ti6O14 gave a positive effect on the lector chemical properties and also obtained that the sample with the smallest ratio exhibited the best performance in charge discharge process. The conductivity of Na2Li2Ti6O14/oC was achieved by the smallest amount of coated carbon with a ratio of 12:1 [10].
- Self-supported Nano arrays enable ultra-high power densities as a result of their open pore geometry, which results in short and direct Li+-ion and electron pathways Vertically aligned carbon nanotubes (VACNT) on metallic current collectors with low interface resistance are used as current collectors for the chemical solution infiltration of electroactive oxides to produce vertically aligned carbon nanotubes decorated with in situ grown $LiMn_2O_4$(LMO) and $Li_4Ti_5O_{12}$ (LTO) nanoparticles. The production processes steps (catalyst coating, VACNT chemical vapor deposition (CVD), infiltration, and thermal transformation) are all scalable, continuous, and suitable for niche market production to achieve high oxide loadings up to 70 wt %. Due to their unique transport structure, as-prepared nano arrays achieve remarkably high power densities up to 2.58 kW kg 1, which is based on the total electrode mass at 80^{o}C for $LiMn_2O_4$//$Li_4Ti_5O_{12}$ full cells. The tailoring of LTO and LMO nanoparticle size (~20–100 nm) and VACNT length (array height: 60–200 m) gives insights into the rate-limiting steps at high current for these kinds of nano array electrodes at very high C-rates of up to 200 ^{o}C. The results reveal the critical structural parameters for achieving high power densities in VACNT nano array full cells. the concept of VACNT-based nanoarrays proved to be a promising approach for future high power LIBs with a noteworthy peak power density of 2.58 kW kg 1, based on a total electrode mass at 80 ^{o}C for LMO//LTO[11].
- A $Li_4Ti_5O_{12}$/carbon nanotubes/graphene composite has been successfully prepared by a solid-state method. For comparison, pure LTO and $Li_4Ti_5O_{12}$/graphene composite were also synthesized using the same method. The materials were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) to confirm the structure and morphology. The results reveal that LTO particles are well dispersed and wrapped in the graphene sheets with cross- linked carbon nanotubes. The electrochemical results show that theLi4Ti5O12/carbon nanotubes/graphene composite exhibits the best rate capacity, which lead to a charge capacity of 169.0, 168.5, 167.1, 153.2, 144.5, 131.5 mAh g−1 at 0.2, 0.5, 1, 3, 5 and 10 C, respectively between 1 and 3 V (1 C = 160 mAh g−1). The synergistic effect of graphene and carbon nanotubes constructing 3D networks could enhance the electronic conductivity of $Li_4Ti_5O_{12}$ carbon nanotubes/graphene composite [12].
- Lithium-sulfur (Li-S) batteries are among the most

promising candidates for the next-generation energy storage systems. However, challenges regarding the limited sulfur content and areal sulfur loading in the cathode lead to a low areal capacity thatcannot even outperform state-of-the-art lithium-ion batteries, which greatly off setsthe high-energy advantage of Li-S batteries and further hinders their practical use. Here,we theoretically indicated that the electronic conduction efficiency of the sulfur host nanomaterial plays a crucial role in determining the sulfur content, and a highly efficient single-wall carbon nanotube (SWCNT) conductive network was constructed for our proof-of-concept studies, resulting in an unprecedentedly high sulfur content up to 95 wt%. The interwoven SWCNTs not only provide abundant paths for electron and lithium ion transport, but also facilitate polysulfides trapping during sulphur conversion reactions. As a result, a high areal capacity of 8.63 mAhcm-2 was obtained with a high areal sulfur loading of 7.2 mgcm-2, much higher than that of lithium-ion[13].

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- Transition metal oxide based electrodes attract much attention because of their potential to offer high energy density. In this study, we report a binder-free composite anode composed of CuO nanosheets and multi-wall carbon nanotubes for LIBs. This composite anode is fabricated by a cost-effective electrophoretic deposition process followed by facile solution immersion. When tested in a LIB, this composite anode delivers a high reversible capacity of 540 mAhg-1 and maintains its capacity retention of above 78% after 50 cycles at a current density of 100 mA g-1, which is much higher than the CuO anode without carbon nanotubes. The high capacity, enhanced rate capability, low resistance, and increased operational life architecture of the hybrid electrode. The carbon nanotubes facilitate the electron transfer, enhance the structural stability of CuO nanosheets, and improve the adhesion of the CuO nanosheets to current collector [14].
- MnO has attracted wide attentions owing to its theoretically high Li-storage capacity, lower working voltage and polarization than other oxides, low cost, environmental friendliness, and abundant resources. Herein, we develop a facile and low-cost strategy to fabricate a unique porousMnO@N-doped carbon (MnO@N-C) nanotube and demonstrate its outstanding Li-storage properties as anode material for LIBs. Benefiting from its unique 1D porous features, the prepared MnO@N-C electrodes exhibit high reversible specific capacity (971.8 mAh g-1 at 0.1 Ag-1), superb high-rate capability (359.5 mAhg-1 at 30 Ag-1) and remarkable cycling stability (441.5 mAh g-1 after 3500 cycles at 10 Ag-1). Such superior electrochemical performance should be due to the high conductivity and protection effects of N-doped carbon layer, and adequate internal voids in the MnO@N-C to effectively accommodate the volume changes of MnO during cycling. In addition it is also disclosed that the high capacity contribution arises from the pseudo capacitive charge storage [15].
- Carbon nanotube (CNT) a promising active material for lithium ion batteries, the relatively low theoretical specific capacity (372 mAhg-1) of CNT has hindered its application. Here we have developed a general and efficient template strategy in synthesizing a new family of CNTs with controllable hollow walls and explored their promising applications in LIBs. The hollow structure formed between CNT core and nitrogen-doped graphene shell can be effectively used for lithium storage, and a reversible specific capacity of 635 mAhg-1 was achieved as anode material in LIB. Interestingly, the hollow structure has been further incorporated with silicon to offer even higher specific capacity of 930mAhg-1 with good cyclic stability [16].
- Seeking free volume around nanostructures for silicon-based anodes has been a crucial strategy to improve cycling and rate performance in the next generation Li-ion batteries. Herein, through a simple pyrolysis and insitu polymerization approach, the low cost commercially available melamine foam as a soft template converts carbon nanotubes into highly dispersed and three-dimensionally inter connected frame work with capsulated silicon/polyaniline hierarchical nano architecture. This unique core-sheath structure based on carbon nanotubes foam integrates a large number of mesoporous, thus providing well-accessible space for electrolyte wetting, whereas the carbon nanotubes matrix serves as conductive thoroughfares for electron transport. Meanwhile, the outer polyaniline coated on silicon nanoparticles provides effective space for volume expansion of silicon, further inhibiting the active material escape from the current collector. As expected, the PANI-Si@CNTs foam exhibits a high initial specific capacity of 1954 mAh g−1 and retains 727 mAh g−1 after 100 cycles at 100 mA g−1, which can be attributed to highly electrical conductivity of carbon nanotubes and protective layer of polyaniline

sheath, together with three-dimensionally interconnected porous skeleton. This facile structure can pave a way for large scale synthesis of high durable silicon-based anodes or other electrode materials with huge volume expansion [17].

- ZnO nanorod was first synthesized via a simple hydrothermal method. Subsequently, the material was annealed with a carbon precursor, forming free-standing, carbon-coated ZnO nanotubes. The carbon-coated nanotube structure is beneficial to alleviate volume changes of the ZnO active material during Li insertion and extraction processes as well as to improve the electrochemical reaction kinetics. Electrochemical test results demonstrate that the carbon-coated ZnO nanotube electrodes deliver improved the cycling performance compared with ZnO nanorod electrodes. Better rate performance than carbon-coated ZnO nanoparticle electrodes was also achieved. FE-SEM, HR-TEM, XRD, and Raman analysis results confirmed the formation of carbon-coated ZNT structures. Electrochemical test results revealed that the carbon-coated ZNT electrode exhibited improved cycling stability with the reversible capacity of approximately 400 mAh g−1 and better rate-performance than the carbon-coated ZnO nanoparticle electrode. These results could be attributed to the role of the carbon-coating layer and nanotube structures: the carbon-coating layer acted as a buffer medium for volume changes of ZnO active materials and provided an electronic conducting path, and the nanotube structure was beneficial for alleviating volume changes by internal space and for fast reaction kinetics by providing internal and external surfaces to contact electrolyte [18].
- Here, we report on the synthesis of single wall carbon nanotube (SWNT)-bridged molybdenum trioxide (MoO3) Nano sheets as anode material for LIBs. We exploit liquid phase exfoliation of layered MoO3 crystallites to produce multilayer MoO3 Nano sheets dispersed in isopropanol, which are then mixed with solution processed SWNTs in the same solvent. The addition of SWNTs to the MoO3 Nano sheets provides the conductive framework for electron transport, as well as a bridge structure, which buffers the volume expansion upon litigation/de-litigation. We demonstrate that the hybrid SWNT-bridged MoO3 structure is beneficial for both the mechanical stability and the electrochemical characteristics of the anodes leading to a specific capacity of 865 mAh g−1 at 100 mA g−1 after 100 cycles, with a columbic efficiency approaching 100% and a capacity fading of 0.02% per cycle. The low-cost, nontoxic, binder-free hybrid MoO3/SWNT here developed represents a forward for the applicability of exfoliated MoO3 in LIB anodes, delivering high energy and power densities [19].
- A novel nanostructured carbon thin film, is synthesized by electron cyclotron plasma enhanced chemical vapor deposition and is proposed as the anode material for lithium ion battery. The individual nanostructures of the thin film have a multiwalled carbon nanotube, with carbon films attached to it, giving it a tree like appearance. All the nanostructures are aligned perpendicular to the surface of the substrate. The unique morphological structure and the vertical alignment provides for a large as well as unhindered area of interaction between the electrode material and the electrolyte. The cyclic voltammetry studies of the material with respect to lithium, shows that the lithium ions can be repeatedly intercalated and deintercalated to and from the material. On performing galvanostatic charge discharge cycling, the material has shown a lithiation capacity of 323 µAh.cm-2.µm-1 (2590 mAh.g-1) and a delithiation capacity of 65 µAh.cm-2.µm-1 (522 mAh.g-1) for the first cycle. The specific capacity after five cycles, during lithiation is 74 µAh.cm-2. µm^{-1}(607 mAh. g^{-1}) delithiation is 56 µAh.cm-2.µm-1 (459 mAh.g-1). The reversible specific capacity for the material remains almost constant after this initial capacity loss up to 50 cycles [20].

3. Working methodology

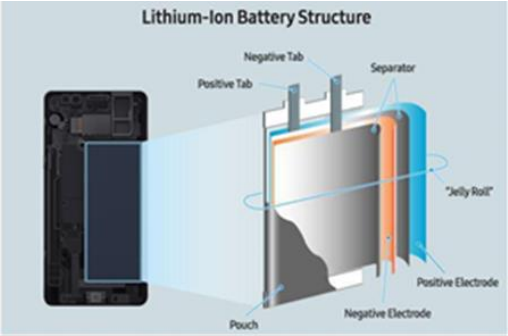

Fig. 3. Construction of lithium ion battery

A. *Fabrication of electrode (li-ion)*

Lithium titanate powders were synthesized by In brief, a stoichiometric amount of anatase-TiO2, Li2CO3 and anhydrous ethanol were mixed by ball milling at 300 rpm for 15 h using zirconia by milling media, the mass ratio of the material to zirconia balls is to be 1:20. The mixture was dried at 85°C for 5 h. The mixed solid powders were calcined at 800°C for 10 h in an air atmosphere to obtain pure LTO. The molar ratio of Li:Ti was 4:5 and excessive Li (5%) was added to compensate for the volatilization of Li during the calcined process. Graphene and carbon nanotubes powders were purchased. For fabricating LTO/carbon nanotubes/graphene composite: 5% wt. graphene and 5% wt. carbon nanotubes were dispersed in anhydrous ethanol with sonication for 0.5 h. Then, the carbon nanotubes and graphene suspension and LTO powders were mixed by ball milling (the weight percentage ratio of the total carbon nanotubes and graphene to LTO is 10%) at 500 rpm for 5 h. Subsequently, the mixture was dried at 85°C for 4 h, followed by calcining at 500°C for 5 h under N2 atmosphere to obtain the homogeneous LTO/carbon nanotubes/graphene composite (abbreviated for LTO-CNT-G). For comparison, a LTO/graphene composite (the weight percentage ratio of graphene to LTO is 10%) was also prepared by the same. This composite was abbreviated LTO-G. Powder XRD with Cu Kα radiation was used to identify the phase composition for all samples. The diffraction patterns were collected at room temperature by scanning stepwise in the range of 10–90° at a scanning rate of 0.02° per 10 s. The morphology of the materials was characterized by SEM.

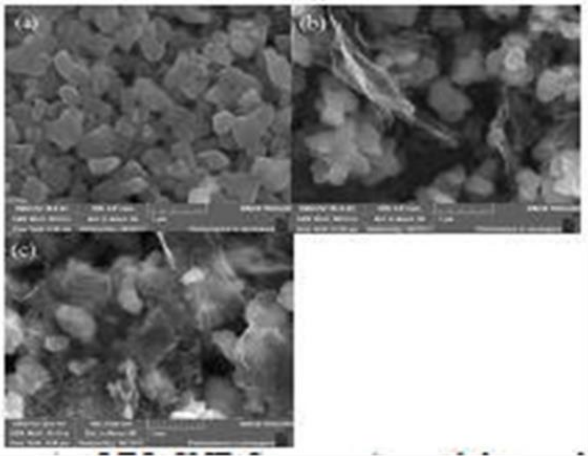

Fig. 4. SEM images of (a) pure LTO, (b) LTO-G and (c) LTO-CNT-G composites.

B. Electrochemical properties

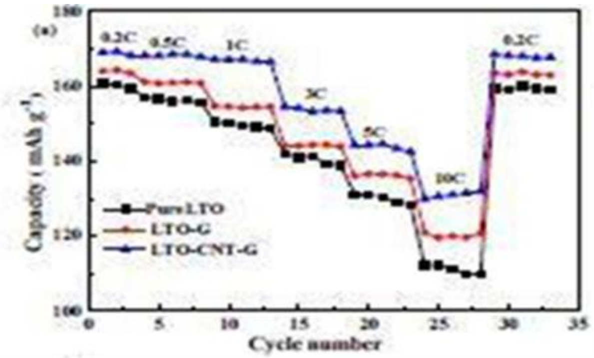

Fig. 5(a). Cycle number vs. capacity

LTO-CNT-G composite exhibits a smallest potential difference between the charge and discharge platforms compared with LTO-G composite and pure LTO at high C-rates. This is attributed to that LTO particles incorporated with graphene and carbon nanotubes could improve electronic conductivity and reduce electrode polarization, thereby enhancing the rate capacity of LTO. The charge capacity values of the LTOCNT-G composite are 169.0, 168.5, 167.1, 153.2, 144.5, 131.5 mAh g−1 at 0.2, 0.5, 1, 3, 5 and 10 C, (1C = 160 mAhg−1), respectively. However, the charge capacity values of the LTO-G composite are 164.3, 160.9, 154.6, 144.3, 136.2, 120.0 mAhg−1, respectively, and the charge capacity values of pureLTO are 160.3, 155.9, 149.5, 139.2, 130.4, 111.1 mAh g−1, respectively.

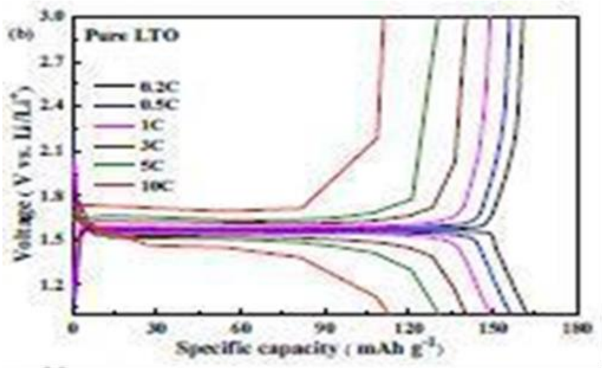

Fig. 5(b). Specific capacity vs. voltage (Pure LTO)

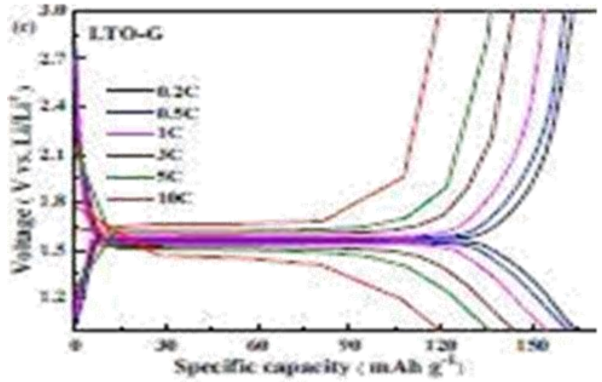

Fig. 5(c). Specific capacity vs. voltage (LTO-G)

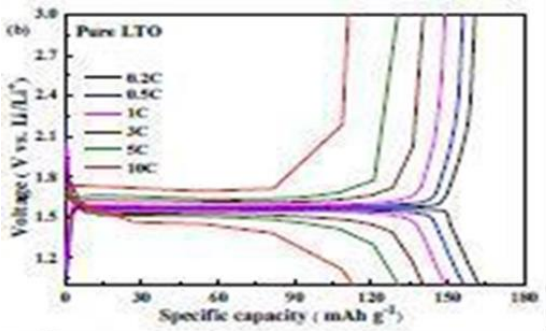

Fig. 5(d). Specific capacity vs. voltage (Pure LTO)

Fig. 5. (a) Rate capacity of pure LTO, LTO-G and LTO-CNT-G composites from 0.2 C to 10C, and (b-d) galvanostatic charge-discharge curves at different C-rates for pure LTO, LTO-G composite, LTO-CNT-G composites between 1 and 3 V (1 C = 160 mAh g^{-1}).LTO-CNT-G composites.

4. Conclusion

In summary, the LTO-CNT-G composite has been successfully reviewed by a solid-state method. The characterization results show that LTO particles are well dispersed and wrapped in the graphene sheets with cross-linked carbon nanotube. The electrochemical results indicate that the LTO-CNT-G composite displays a superior rate capability than the LTO-G composite and pure LTO, which may be attributed to that the synergistic effect of graphene and carbon nanotubes could enhance the electronic conductivity and reduce electrode polarization. Therefore, the LTO-CNT-G composite is a promising anode material for lithium ion batteries.

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