

Scandium and niobium incorporated lithium titanate as the anode for Li-ion batteries

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Scandium and Niobium doped Lithium Titanate is prepared by a sol-gel technique based on the formula $\text{Li}_{4-x}\text{Sc}_x\text{Ti}_{5-y}\text{Nb}_y\text{O}_{12}$, where $x = y = 0.0$ & 0.3 i.e. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_{3.7}\text{Sc}_{0.3}\text{Ti}_{4.7}\text{Nb}_{0.3}\text{O}_{12}$. The specific capacity of Sc and Nb incorporated LTO has been observed as 227.5 mAhg^{-1} at 1 c, while this value has shown a decrease in the value of the specific capacity of the electrode i.e. 105.5 mAhg^{-1} at 20 c even after many test cycles. It has also been observed that Sc-Nb doping is suitable for the reversible cycle of the battery system and the extraction of Li^+ .

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1. Introduction

Lithium-ion batteries have shown highly useful as a power source in the field of portable electronic devices, hybrid electric vehicles, or as energy storage. Fast depleting fossil fuel makes the development and gradation of alternative energy sources such as Lithium-ion batteries essential. Lithium-ion source has emerged as highly safe energy and it has high energy density at small volume. Lithium-ion batteries having spinal structure $\text{Li}_4\text{Ti}_5\text{O}_{12}$, commonly refer as LTO have demonstrated better energy density and other battery features in comparison to currently graphite-based batteries [1-3]. One of the most important features of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is its zero strain material features. Zero strain material feature means there is no change in the unit cell volume of LTO after the extraction or insertion of Lithium-ion during the life cycle of the battery [5]. One another feature of the LTO battery that makes it better than others existing is its very flat voltage plateau at $1.55 \text{ V Vs Lt/ Li}^+$, this value is higher than the reduction potential of most of the organic electrolytes. Thus Lithium-ion cell such as LTO has been found as more stable and safer than other carbon-based material battery.

Despite all the advantages of the LTO mentioned in the above column, there are a few challenges that require addressing by the scientific community. The first challenge is its low electronic conductivity, which makes it a low-rate capacity battery. The second challenge is related to LTO's low specific capacity at various Columbic values. The third challenge addressed in this paper is related to low discharge capacity at various cycle numbers of the battery. These three issues of LTO batteries are addressed in the present research work.

The work strategy to cover above mentioned three issues of LTO battery is based on the selection of proper material fabrication and selection of proper additives or incorporating material. The sol-gel technique of powder preparation has been adopted to prepare the material. As per the literature survey, the double doping of Scandium and Niobium has been selected.

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2. Experimental

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_{3.7}\text{Sc}_{0.3}\text{Ti}_{4.7}\text{Nb}_{0.3}\text{O}_{12}$ based on the stoichiometric formula $\text{Li}_{4-x}\text{Sc}_x\text{Ti}_{5-y}\text{Nb}_y\text{O}_{12}$ were synthesized by the chemical method of sol-gel technique. Lithium acetate (CH_3COOLi), titanium nitrate ($\text{Ti}(\text{NO}_3)_4$), niobium hydroxide ($\text{Nb}(\text{OH})_5$), and Scandium hydroxide ($\text{Sc}(\text{OH})_3$) had been taken as the base material as per the stoichiometric formula. The gel obtained was dried at 120°C for 8 hours to evaporate the residue of ethanol and other volatile materials. The colour of the powder was light blue. The pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was also prepared adopting a similar fabrication route. The powder obtained was calcined at 800°C for one hour to make the material in the proper phase of LTO.

X-ray diffraction (XRD) analysis of the material had been done with the help of a Rigaku XRD machine using Cu – k alpha radiation in the 2 theta range of 10° to 80° .

The electrochemical property of the pure and Sc-Nb doped LTO battery was determined by taking the help of coin cells [24-25]. A mixed solvent of dimethyl carbonate and ethylene carbonate (1: 1 in volume) having 1 mol dm^{-3} LiPF_6 was taken as an electrolyte. Polypropylene membrane was used as the separator in the cell. The electrodes were fabricated by active material and carbon black and the binder polyvinylidene fluoride in the ratio of 82:10:8. The slurry of electrode mixture was coated on a copper current collector. Lithium metal was used as the counter electrode.

Electrochemical tests were carried out at room temperature. Charge–discharge cycle tests were performed in the voltage range of 0.5 V to 3.5 V using a battery testing system. An electrical resistance test of sintered electrode material was also carried out with the help of an impedance analyzer.

3. Results and discussions

Fig.1 shows the XRD micrograph of $\text{Li}_{3.7}\text{Sc}_{0.3}\text{Ti}_{4.7}\text{Nb}_{0.3}\text{O}_{12}$. The diffraction peaks confirm the cubic spinel structure as per the matching with JCPDS card number 49-0207.

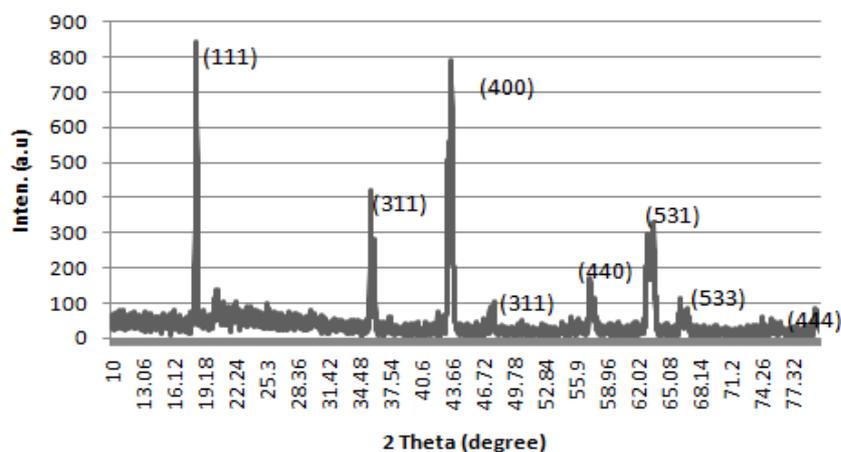


Fig. 1. XRD micrograph of $\text{Li}_{3.7}\text{Sc}_{0.3}\text{Ti}_{4.7}\text{Nb}_{0.3}\text{O}_{12}$.

The hkl value peak (111) is an indication of the shifting of the peak towards a smaller angle due to the incorporation of double dopants. This shifting indicates the enhancement of lattice size due to the incorporation of dopants in undoped lithium titanate [7]. Further, It has been reported [8] that the enhancement of lattice size indicates a decrease in particle size; as a result, there would be an increase in surface stress of the electrode and this finally helps in increasing of discharge capacity of the cell. This has been experimentally found true and it is discussed in successive below column.

The crystallite size of the modified LTO i.e. $\text{Li}_{3.7}\text{Sc}_{0.3}\text{Ti}_{4.7}\text{Nb}_{0.3}\text{O}_{12}$ was calculated by using the Scherrer formula and it was calculated as 180 nm. The lattice constant was obtained as 8.367 \AA .

Fig.2 shows the Scanning Electron Microscopy (SEM) image of $\text{Li}_{3.7}\text{Sc}_{0.3}\text{Ti}_{4.7}\text{Nb}_{0.3}\text{O}_{12}$ powder converted into a pellet shape applying a pressure of 180 MPa by using a hydraulic press and sintered at 800°C for one hour. The selection of sintering temperature and pressure is aimed to produce optimum densification in the material and suitability for a better electrode [9-10]. SEM image shows clear and distinguished formation of grains in the material. The average grain size in sintered $\text{Li}_{3.7}\text{Sc}_{0.3}\text{Ti}_{4.7}\text{Nb}_{0.3}\text{O}_{12}$ is observed to be $15 \mu\text{m}$.

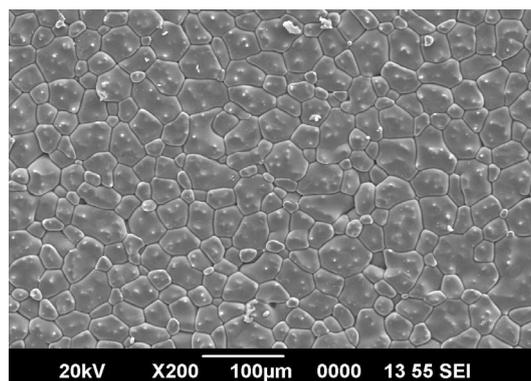


Fig. 2. SEM micrograph of $\text{Li}_{3.7}\text{Sc}_{0.3}\text{Ti}_{4.7}\text{Nb}_{0.3}\text{O}_{12}$ pellet sintered at 800°C for 1-hour.

The specific capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode is tested and it is shown as the charge-discharge curve in Fig.3. The charge discharge curve of the improved lithium titanate electrode i.e. $\text{Li}_{3.7}\text{Sc}_{0.3}\text{Ti}_{4.7}\text{Nb}_{0.3}\text{O}_{12}$ is displayed in Fig.4. To compare the changes in specific capacity of the parent and the doped electrode, same range of current i.e. from 1 C to 20 C was applied in both the electrode to study the charging-discharging capability. It has been observed from Fig. 3 and Fig.4 that the specific capacity of the electrode decreases with the increase in current density. This is due to decreases in the penetration of ions in the inner pore due to fast potential change or potential hikes [11-12]. Comparison of the specific capacity of pure and doped lithium titanate electrodes reveals that at 1 C there is increase in specific capacity by 7.98 % (from 213 mA/g to 230 mA/g) due to the incorporation of double dopant (Sc & Nb) in parent lithium titanate electrode.

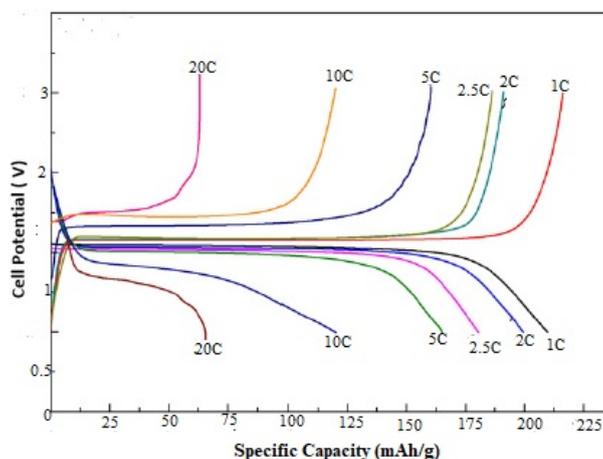


Fig. 3. Specific capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at varying potential.

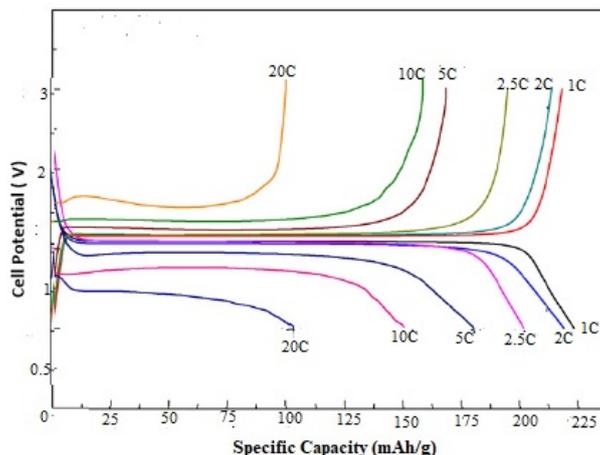


Fig.4. Specific capacity of $Li_{3.7}Sc_{0.3}Ti_{4.7}Nb_{0.3}O_{12}$ at varying potential.

Similar increases in charging – discharging are observed at other higher ranges of current i.e. 2 C, 2.5 C, 5 C, 10 C, and 20 C in the case of $Li_{3.7}Sc_{0.3}Ti_{4.7}Nb_{0.3}O_{12}$ electrode.

Discharge capability with the increase in cycle number is the measure of the life span of a battery electrode. In Fig.5 and Fig.6, the changes in discharge capacity of pure PTO and improved PTO with the increase in cycle number at 2 C and 1 C are shown respectively.

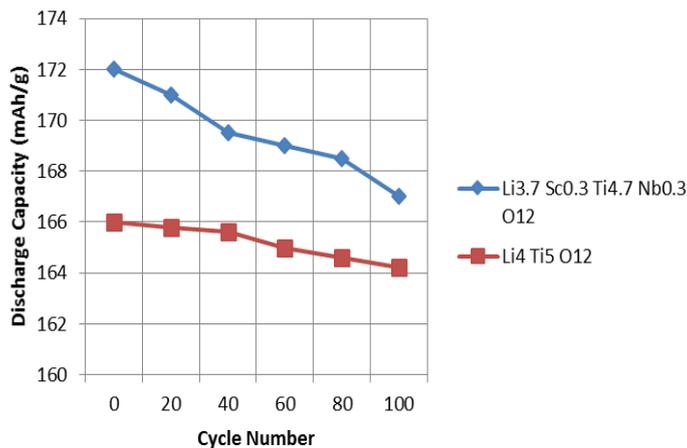


Fig.5. Discharge capacity study at varying Cycle Numbers at 2 C.

Remarkable increases in the discharge capacity of the PTO electrode are observed after the incorporation of dopants. An increase of 1.82% discharge capacity at 2 C and 7.1% increase in discharge capacity at 1 C are observed after the incorporation of dopants even at 100 cycles. The result of discharge capacity with cycle number obtained in $Li_{3.7}Sc_{0.3}Ti_{4.7}Nb_{0.3}O_{12}$ is compared to other similar results reported by various authors [13-15].

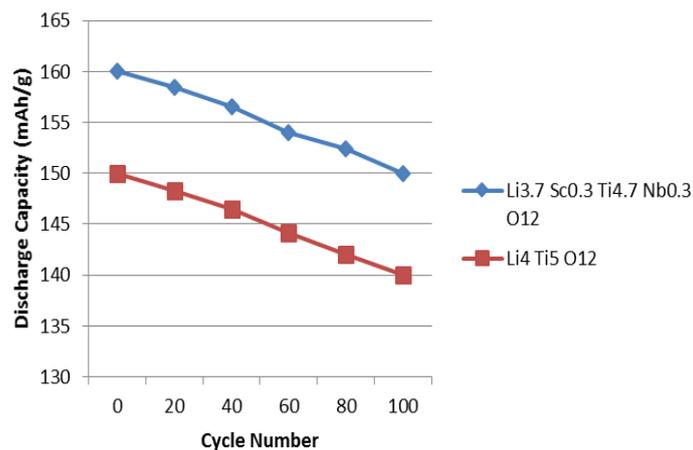


Fig.6. Discharge capacity study at varying Cycle Numbers at 1 C.

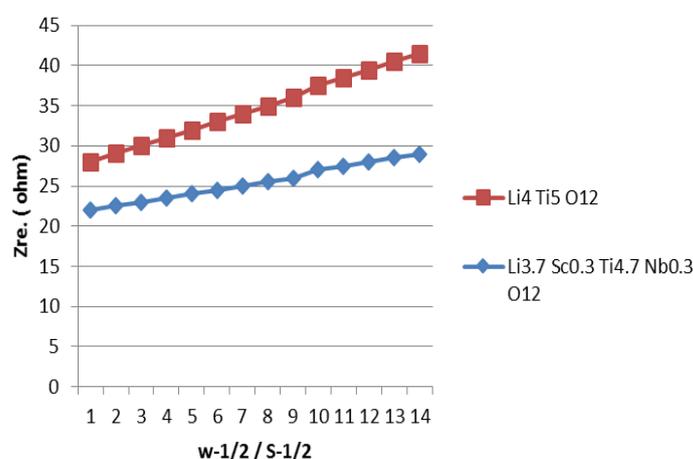


Fig.7. Real impedance with the low frequency of Pure LTO and incorporated LTO.

A comparison of changes of real impedance with the varying low frequency in LTO and incorporated improved LTO is shown in Fig.7. Diffusion impedance characteristics of a chargeable battery is an important parameter and this characteristic is measured by applying low-frequency signals [16-18]. There are considerable decreases in real impedance observed in the case of $\text{Li}_{3.7}\text{Sc}_{0.3}\text{Ti}_{4.7}\text{Nb}_{0.3}\text{O}_{12}$ in comparison to pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$. It reflects that the conductivity of the electrode after incorporation of double dopants i.e. Sc and Nb gets increased, hence there is an increase in conductivity, and better ionic movement among the electrodes is expected.

4. Conclusions

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_{3.7}\text{Sc}_{0.3}\text{Ti}_{4.7}\text{Nb}_{0.3}\text{O}_{12}$ based on the stoichiometric formula $\text{Li}_{4-x}\text{Sc}_x\text{Ti}_{5-y}\text{Nb}_y\text{O}_{12}$ were synthesized by the chemical method of sol-gel technique. XRD micrograph of calcined $\text{Li}_{3.7}\text{Sc}_{0.3}\text{Ti}_{4.7}\text{Nb}_{0.3}\text{O}_{12}$ powders approved the cubic spinal structure. The crystallite size of the modified LTO i.e. $\text{Li}_{3.7}\text{Sc}_{0.3}\text{Ti}_{4.7}\text{Nb}_{0.3}\text{O}_{12}$ was calculated by using the Scherrer formula and it was calculated as 180 nm. The lattice constant was obtained as 8.367 \AA . SEM image of the sintered pellet of $\text{Li}_{3.7}\text{Sc}_{0.3}\text{Ti}_{4.7}\text{Nb}_{0.3}\text{O}_{12}$ shows the clear and distinguished formation of grains in the material. The average grain size in sintered $\text{Li}_{3.7}\text{Sc}_{0.3}\text{Ti}_{4.7}\text{Nb}_{0.3}\text{O}_{12}$ was observed to be $15 \mu\text{m}$. The specific capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Sc-Nb modified $\text{Li}_{3.7}\text{Sc}_{0.3}\text{Ti}_{4.7}\text{Nb}_{0.3}\text{O}_{12}$ are tested and it is shown as the charge-discharge curve in the above text. The specific capacity of the electrode

decreases with the increase in current density. This is due to decreases in the penetration of ions in the inner pore due to fast potential change or potential hike.

A comparison of the specific capacity of pure and doped lithium titanate electrodes revealed that at the 1 C there is increase in specific capacity by 7.98 % (from 213 mA/g to 230 mA/g) due to the incorporation of double dopant (Sc & Nb) in parent lithium titanate electrode. Remarkable increases in the discharge capacity of the PTO electrode are observed after the incorporation of dopants. An increase of 1.82% in discharge capacity at 2 C and 7.1% increase in discharge capacity at 1 C are observed after the incorporation of dopants even at 100 cycles. There are considerable decreases in real impedance observed in the case of $\text{Li}_{3.7}\text{Sc}_{0.3}\text{Ti}_{4.7}\text{Nb}_{0.3}\text{O}_{12}$ in comparison to pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$. It reflects that the conductivity of the electrode after incorporation of double dopants i.e. Sc and Nb gets increased, hence there is an increase in conductivity, and better ionic movement among the electrodes is expected. All the findings indicate that $\text{Li}_{3.7}\text{Sc}_{0.3}\text{Ti}_{4.7}\text{Nb}_{0.3}\text{O}_{12}$ electrodes may be a competent anode for a lithium-ion battery.

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