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Sol-gel assisted spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and its performance and stability as anode for long life Li-ion battery

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Abstract: Li-ion batteries are extensively used in portable electronics due to high energy, power density and superior electrochemical performance. For this, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ a zero strain anode material with excellent reversibility for the Li-ion insertion and de-insertion and flat potential plateau, serves as an ideal anode material. However, it has low conductivity which hampers its commercialization. In the present work, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is prepared by sol-gel method. Its structural analysis confirms the formation of nanoparticles with uniformly aligned grains and exhibits high discharge capacity of 181 mA.h/g at 0.1 C. It is the synergetic effect of nanoparticles size and surface area, which imparts it the outstanding electrochemical performance in terms of long term stability and charge storage capacity.

Key words: Electroceramics; Energy storage and conversion; Nano crystalline materials; Sol-gel preparation; X-ray techniques

1. Introduction: An ever-growing use of portable devices demands more efficient and high energy density storage devices. Li-ion batteries (LIBs) are potential candidates because of the attractive features like light weight, appropriate potential and energy density [1]. The energy and power densities of battery and its electrochemical performance are governed by the

physiochemical properties of the anode materials. Generally, graphite is used as an anode. However, during electrochemical reaction, lithium dendrites are formed on the surface of graphite, which results in the internal short circuit and hence creating safety issues. Therefore, there is need to develop high performance anode materials.

Titanium based binary and ternary oxide materials have been pursued as an alternative for the next generation LIBs due to their structural stability, cost effectiveness, low toxicity and excellent electrochemical performance [2]. Among the titanium based active materials, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is zero strain material and exhibits excellent Li-ion insertion de-insertion reversibility with negligible volume change and flat potential plateau [3]. On the other hand, its poor electronic conductivity (10^{-13} S/cm) and moderate Li-ion diffusion (10^{-8} cm^2/s) limits the electrochemical performance [4]. This problem can be alleviated using various strategies like reducing particle size [5], metal ion doping [6] and cold press compacting [7]. Decreasing of particle size leads to minimization of diffusion path along with enhanced contact between active material and electrolyte [8-10]. In view of this, synthesis of nano-structured material is the cost effective way to enhance the electrochemical performance.

Moreover, the desired purity, morphology, particle size and homogeneity are achieved by choosing the suitable synthesis method among hydrothermal [11], sol-gel [3], solid state [12] and spray draying [13]. Lithium titanate synthesized by solid state route is also reported to suffer from local heterogeneity [14], an issue which can be addressed sol-gel method. We in this work employ a facile sol-gel method for better control over reaction conditions, which offers phase pure, homogeneous and smaller particles. A half-cell has also been assembled to demonstrate excellent electrochemical performance.

2. Experimental:

2.1 Synthesis of Lithium Titanate: $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was prepared using lithium acetate and titanium isopropoxide as starting materials. Lithium acetate was obtained by adding Li_2CO_3 in glacial acetic acid in stoichiometric ratio and diluted by addition of acetic acid, isopropanol and water in 1:1:1 ratio. Then titanium isopropoxide was dissolved in isopropanol and added to above solution by a burette at a controlled rate. The solution was stirred well and kept it in the hot bath till the gel formation. Once the gel was formed, it was pre-calcined at 600°C for 2 hr to confirm whether the compound was formed or not and then heated at 800°C for 2hr.

2.2 Fabrication of Electrode: In order to prepare the anode, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, carbon black and PVDF (Polyvinylidene fluoride) were mixed in N-methyl-2-pyrrolidone (NMP) medium. The weight ratio of the three was kept 75:15:10 respectively. The slurry obtained by above mixing was applied on copper foil by doctor blade method. The resultant film was dried at 120°C for 12 hrs and circular discs with 16 mm diameter were punched out of this film. A lithium metal foil was used as counter electrode and celgard 2400 membrane was used as separator, while LiPF_6 in ethylene carbonate, diethyl carbonate and dimethyl carbonate (Ratio 1:1:1) was used as electrolyte. Inert atmosphere (Argon) glove box was used for assembling the coin type half-cell. Biologic-108 battery cycler was used to evaluate the electrochemical performance of the cell. The performance was evaluated in terms of galvanostatic charge discharge and cyclic voltammetry in 0.1-2.5 V range. The voltage in the above-mentioned voltage range was recorded with respect to Li/Li^+ .

3. Result and discussion:

3.1 Characterization of $\text{Li}_4\text{Ti}_5\text{O}_{12}$: As prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$ obtained from sol-gel method was heat treated at different temperatures. The powder heated at 600°C shows a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase but with unidentified impurity at 59.5° . Therefore, powder was again heated at 800°C for 4hr to

improve its purity and crystallinity. Fig. 1 shows the XRD pattern of sample heated at 800°C. The observed diffraction peaks match with JCPDS card no. 26-1198, for single phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ($a = 8.43\text{\AA}$). Scherrer formula was used to calculate the crystallite size. The observed crystallite size for 111 plane is ~54 nm.

Electron micrographs of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ are shown as Fig 1 b & c. The sample showed well-connected spherical particles within 50-200 nm range even after calcination at 800°C. This type of morphology is expected to provide good Li-ion diffusion and improved electrochemical performance.

3.2 Electrochemical performance: Li-ion insertion/de-insertion mechanism of the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was studied by cyclic voltammetry in the potential window 1.0-2.5 V vs Li/Li⁺ at scan rate 0.1 mV/s. Fig. 3a clearly shows a single pair of oxidation and reduction peaks. The cathodic peak observed at 1.5 V can be assigned to the insertion of Li-ion into the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and to the voltage plateau of discharge process of the half-cell. Similarly, the anodic peak observed at 1.64 V can be assigned to the de-insertion of Li-ion from $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and to the voltage plateau of charge process of the half-cell [15]. The observed potential difference (ΔV) is 0.14 V and this small value of ΔV reveals good reversibility of Li insertion and de-insertion [16]. The cyclic voltammetry profiles with various scan rates (0.01, 0.1 and 0.3 mV/s) are also recorded (Fig. 2). An increase in the scan rate resulted into the increase in potential difference due to rise in polarization [17].

The charge storage capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was investigated by recording charge-discharge profile at 0.1C. Inset-I of Fig. 3 reveals that, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has charge and discharge plateau respectively at 1.57 and 1.55V delivering discharge capacity of 183 mA.h/g. The nano size $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles lead to the surface reconstruction [18] and forms $\text{Li}_{7+x}\text{Ti}_5\text{O}_{12}$ on the surface

enhancing the capacity [5]. The tap density of the material was found to be 1.61 gm/cm³ which is comparable to the reported values of 1.56-1.62 gm/cm³ [8, 19], with volumetric capacity of 295 mA.h/cm³ [20]. It can be further enhanced by energy extensive methods like cold pressing etc [7, 20]. Subsequently, the lithium insertion and de-insertion rate was increased step wise up to 50C (Fig. 3). The observed discharge capacities for 0.1, 0.2, 0.5, 1, 2, 5, 10, 20 and 50C were 183, 167, 150, 140, 128, 117, 99, 78 and 47 mA.h/g, correspondingly. The decreasing discharge capacities with increase in current are obviously due to incomplete deintercalation of Li-ions from the anode. In addition, nearly 100 % coulombic efficiency was observed for all applied currents. After evaluating performance at higher current the cell was once more cycled at its initial value (0.1C) and it delivers discharge capacity 181 mA.h/g. The capacity as high as 181 mA.h/g at 0.1 C proves that the Li₄Ti₅O₁₂ produced by this route exhibits excellent electrode functionality and also stability.

In order to further examine the cycling stability and capacity fading, Li₄Ti₅O₁₂ was cycled at 0.2C upto 200 cycles. The plot of discharge capacity and columbic efficiency as a function of cycle number is shown in Inset-II of Fig. 3. The observed discharge capacity is 176 mA.h/g for the first cycle and 168 and 165 mA.h/g after 50 and 200 cycles respectively. After 200 cycles, 93 % capacity retention is observed with 100 % coulombic efficiency demonstrating excellent structural stability and high purity.

4. Conclusion: In conclusion, Li₄Ti₅O₁₂ powder obtained by sol-gel technique is single phase with crystallite size of ~54 nm. At lower current (0.1C), Li₄Ti₅O₁₂ exhibited its theoretical capacity of 183 mA.h/g. Even after 200 cycles it delivers 93 % of its initial capacity at 0.2 C. Thus Lithium titanate obtained by sol-gel is phase pure and structurally stable and can be used for long cycle life applications.

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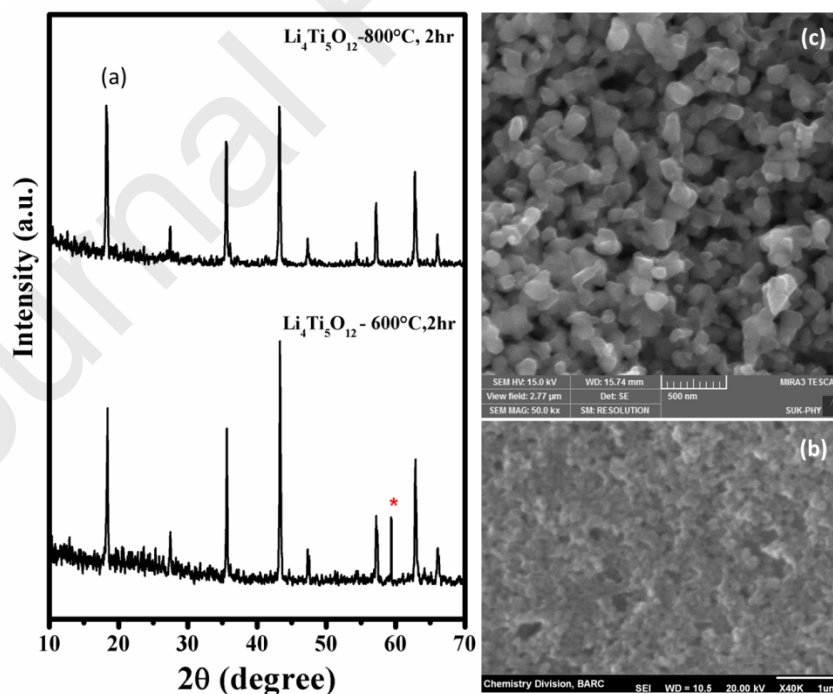


Fig.1: XRD pattern (a) and Micrograph after 600°C (b) and 800°C (c) heating.

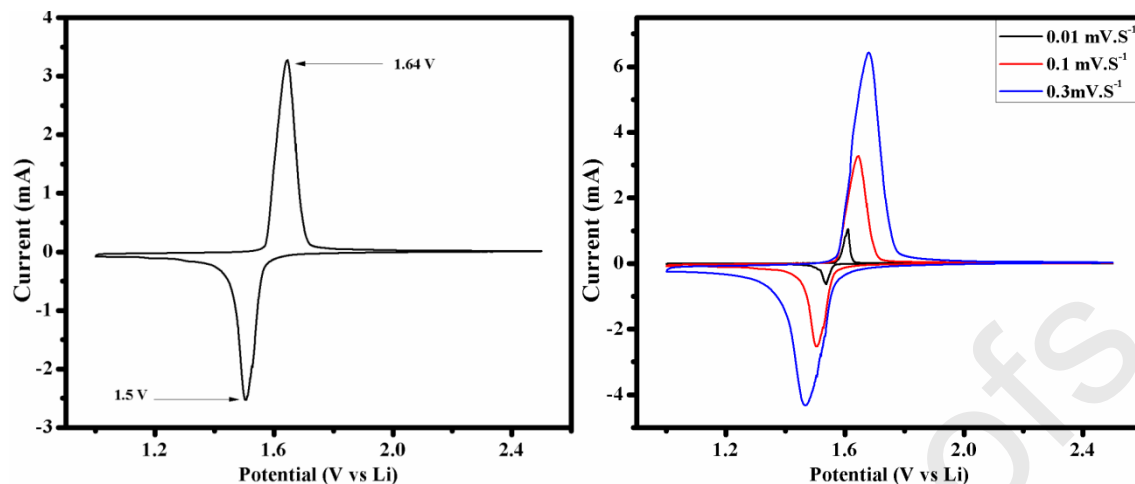


Fig. 2: Cyclic voltammetry profile of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at (a) 0.1 mV s^{-1} and (b) 0.01 , 0.1 and 0.3 mV s^{-1}

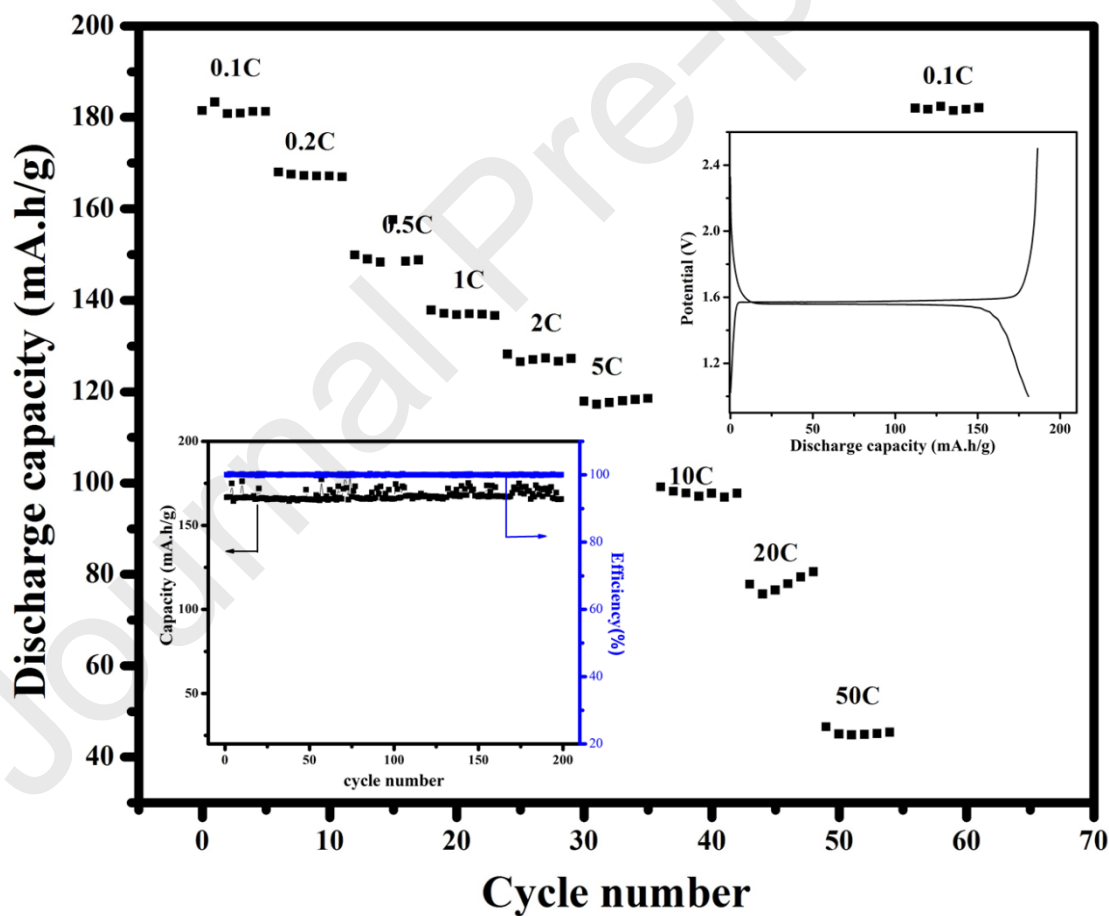


Fig. 3: Performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at various C rates (Inset I: Charge-discharge profile at 0.1C and Inset II: Specific capacity and columbic efficiency as a function of cycle number)

S. J. Rajoba: Investigation, Writing - Original Draft, **Ajit N. Shirsat:** Investigation, **Deepak Tyagi:** Investigation, Writing - Original Draft, **L. D. Jadhav:** Conceptualization, Writing - Review & Editing, Funding acquisition, **R. S. Kalubarme:** Investigation, **B. N. Wani:** Supervision, Funding acquisition, **S. Varma:** Conceptualization, Writing - Review & Editing

Highlights:

1. Facile synthesis of single phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ by sol-gel route.
2. Particle size controlled to 50-200 nm.
3. Exhibits capacity of 183 mA.h/g at 0.1 C
4. Even after 200 cycles it delivers 93 % of its initial capacity at 0.2 C.