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Electrochemical Characteristics and Li⁺ Ions Intercalation Kinetics of Dual-Phase Li₄Ti₅O₁₂/Li₂TiO₃ Composite in Voltage Range of 0–3 V

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ABSTRACT: Li₄Ti₅O₁₂, Li₂TiO₃ and dual-phase Li₄Ti₅O₁₂/Li₂TiO₃ composite were prepared by sol-gel method with average particle size of 1 μm, 0.3 μm and 0.4 μm, respectively. Though Li₂TiO₃ is electrochemically inactive, the rate capability of Li₄Ti₅O₁₂/Li₂TiO₃ is comparable to Li₄Ti₅O₁₂ at different current rates. Li₄Ti₅O₁₂/Li₂TiO₃ also shows good rate performance of 90 mA h g⁻¹ at high rate of 10 C in voltage range of 1–3 V, attributable to increased interfaces in the composite. While Li₄Ti₅O₁₂ delivers capacity retention of 88.6 % at 0.2 C over 50 cycles, Li₄Ti₅O₁₂/Li₂TiO₃ exhibits no capacity fading at 0.2 C (40 cycles) and capacity retention of 98.45 % at 0.5 C (50 cycles). This highly stable cycling performance is attributed to the contribution of Li₂TiO₃ in preventing undesirable reaction of Li₄Ti₅O₁₂ with the electrolyte during cycling. CV curves of Li₄Ti₅O₁₂/Li₂TiO₃ in 0–3 V range exhibit two anodic peaks at 1.51 V and 0.7–0.0 V, indicating two modes of lithium intercalation into the lattice sites of active material. Owing to enhanced intercalation/de-intercalation kinetics in 0–3 V, composite electrode delivers superior rate performance of 203 mAh/g at 2.85 C and 140 mAh/g at 5.7 C with good reversible capacity retention over 100 cycles.

■ INTRODUCTION

Rechargeable lithium-ion batteries are a promising energy source over other traditional rechargeable battery systems due to high output voltage, large energy density and being environment friendly. Li₄Ti₅O₁₂ has attracted widespread attention as anode material in high power lithium-ion rechargeable batteries and hybrid super capacitors owing to their good cyclability, safety at high current rates and long cycle life.¹⁻² It bears excellent cyclability with almost no volume expansion in the unit cell in the process of lithiation.²⁻³ Moreover, its high

operating voltage i.e. 1.55 V (vs. Li/Li^+) makes it safe for high current rates as compared to commercial carbonaceous anodes operating around 0.1 V. This high voltage also makes $\text{Li}_4\text{Ti}_5\text{O}_{12}$ chemically compatible with the electrolytes as solid electrolyte interface (SEI) films form while operating below 1 V.⁴

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ has a stable $[\text{Li}_3]^{8a}[\text{Li}_1\text{Ti}_5]^{16d}[\text{O}_{12}]^{32e}$ framework, where all tetrahedral (8a) sites and 1/6 of the 16d sites are taken by Li atoms, while 5/6 of the 16d sites are occupied by Ti atoms. Oxygen atoms reside at 32e sites. The octahedral (16c) sites are empty. Theoretically, a maximum of 3 lithium ions per formula unit can be accommodated in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ fully occupying the 16c sites, with theoretical capacity of 175 mA h g^{-1} , when discharged to 1 V.⁵ In Li-intercalated $\text{Li}_7\text{Ti}_5\text{O}_{12}$ structure the additional three Li atoms occupy the octahedral (16c) sites. Besides, the tetrahedral (8a) Li atoms also move to the octahedral (16c) sites. Hence, $\text{Li}_7\text{Ti}_5\text{O}_{12}$ represents a structure denoted as $[\text{Li}_6]^{16c}[\text{Li}_1\text{Ti}_5]^{16d}[\text{O}_{12}]^{32e}$, providing interstitial 8a tetrahedral and 16c octahedral spaces for transport of Li^+ ions.² Zhong et al. explored the possibility of further lithium storage into the empty 8a sites of $\text{Li}_7\text{Ti}_5\text{O}_{12}$ by first principle calculations.⁶ The authors predicted that pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can bear the theoretical capacity of 262 mAh/g transforming to $\text{Li}_{8.5}\text{Ti}_5\text{O}_{12}$ when discharged to 0 V. Lithiation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to $\text{Li}_{8.5}\text{Ti}_5\text{O}_{12}$ at 8a sites accompanies a small lattice expansion of about 0.4 % which makes the charging/discharging process reversible without distortion of the spinel $[\text{Li}_1\text{Ti}_5]^{16d}[\text{O}_{12}]^{32e}$ framework. This expansion is much small as compared to other intercalation electrode materials of lithium-ion batteries. Zhong et al. also predicted Li-intercalation potentials of 1.48 V and 0.05 V (vs. Li/Li^+) for crystal transformation from $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to $\text{Li}_7\text{Ti}_5\text{O}_{12}$ and $\text{Li}_7\text{Ti}_5\text{O}_{12}$ to $\text{Li}_{8.5}\text{Ti}_5\text{O}_{12}$ compositions, respectively.

In spite of the promising features of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes, achieving high power density (high current rate capability) is still impeded by low lithium diffusion coefficient $\sim 10^{-9} \text{ cm}^2/\text{s}$ ⁷ and electrical conductivity $\sim 10^{-9}$ – 10^{-7} S/cm .⁸ Irreversible capacity loss at high current rates, is mainly due to slow diffusion of lithium-ions and electrons into the electrochemically active material.⁹ In the field of batteries, current research is mainly focused on exploring high energy density i.e. good reversible capacity and enhanced capacity retention at high current rates. In this regard, many strategies have been developed including tuning the morphologies and architectures¹⁰⁻¹³, particle size reduction to nano-size¹⁴⁻¹⁵, substituting suitable dopants like Mg, Zn, Al¹⁶⁻¹⁸ and making composites with conductive metals i.e. $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ ¹⁹, $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Cu}$ ²⁰, $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNT}$ ²¹. Moreover, binary and multinary compounds (composites) based-anodes like $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{TiO}_2/\text{C}/\text{CNTs}$, N-doped carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Graphite Carbon-Coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ are being extensively studied to benefit from increased grain boundary density with large interfacial areas for high lithium storage.²²⁻²⁶ Large number of grain boundaries provides increased channels for Li-ions to enter the particles. Composites have also been reported to be beneficial for improving the morphological stability of the electrode materials. In last five years, many groups have studied composites of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with metal oxides to explore high rate capability with rich grain boundaries enabling fast diffusion of ions into the active material.²⁷⁻³³ In this regard, $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{TiO}_2$ composites have been extensively studied for electrochemical characteristics, yet $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-Li}_2\text{Ti}_3\text{O}_7$ ³⁴ and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ ²⁵ have only been reported once by Zhu et al. and Wang et al., respectively. Wang et al. reported extraordinary high rate

performance and cycling stability of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite by solid state synthesis, owing to rich grain boundaries.

In the present work, we have synthesized pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$, Li_2TiO_3 and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite, by sol-gel method. We have conducted a comparative study on the structural characterization and electrochemical behavior of these compounds as anode materials for lithium-ion battery in the voltage range of 1–3 V. $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ shows stable cycling performance in comparison with pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Moreover, $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite has also been studied for electrochemical kinetics in voltage range of 0–3 V. $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ shows increased lithium intercalation/de-intercalation with high reversible capacity and good cycling performance when discharged to 0 V.

■ EXPERIMENTAL SECTION

Synthesis. Phase-pure Li_2TiO_3 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite powders were prepared by sol-gel method using Li:Ti molar ratio of 2:1, 4:5 and 4.8:5, respectively. For each sample calculated amount of titanium butoxide was added in the mixture of ethanol absolute and acetic acid (mixture ratio 3:1), followed by stirring for 2.5 hours. Here acetic acid acts as a chelating agent which forms a homogeneous gel that gives rise to narrow particle size distribution and good dispersion after heat treatment. For each sample, weighed quantity of lithium acetate was dissolved in the distilled water, added to the above prepared mixture and stirred for 2.5 hours. The resulting clear gels were dried at 200 °C and white powders were obtained. Phase pure crystalline Li_2TiO_3 and composite $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ were obtained at 800 °C for 3 hours. However $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder calcined for 3 hours contained impurity phases of both TiO_2 and Li_2TiO_3 as shown in the XRD pattern (Supporting information, Figure S1). Sintering the sample for 2 hours resulted into pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which is attributed to the transformation of TiO_2 and Li_2TiO_3 impurities into the desired $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase. Such impurity phases have also been reported by other groups and were removed by long hours heating.³⁵⁻³⁷

Characterization. The crystalline structure and chemical composition of Li_2TiO_3 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite were analyzed by X-ray diffraction (model JDX-11 of Joel Company Ltd., Japan) in the range of 10° to 80° at the scan rate of 0.02° per minute. Morphology of the samples was examined by scanning electron microscope (model JSM-6490A of Joel Company Ltd. Japan) and transmission electron microscope (FEI Company's Titan G260-300CT TEM). The exact phase composition and lattice structures of the samples were characterized by high resolution transmission electron microscopy (HR-TEM) and scanning area electron diffraction (SAED) measurements.

Electrochemical measurements. The electrochemical characteristics of the samples were evaluated by fabricating sealed cells. The working electrodes of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, Li_2TiO_3 and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite were prepared by a slurry coating procedure. The slurries were

prepared by grinding and sonicating 80 wt % of the sample to be examined, 10 wt % acetylene black and 10 wt % polyvinylidene fluoride (PVDF) binder in N-methyl-pyrrolidinone solvent. Binder was first dissolved in the solvent by magnetic stirring and heating at 80 °C. Each sample to be examined was dispersed in N-methyl-pyrrolidinone by ultra sonication. Binder solution was added slowly and the mixture was further sonicated to get uniform slurry. This slurry was uniformly coated on copper foil current collector by brush coating. Several coats were applied to get 3 mg/cm² loading. The working electrodes were dried in vacuum oven at 100 °C for 12 hours. 2025 coin-type half-cell devices were fabricated in argon filled glove box using lithium as counter electrode, polyethylene as separator and 1 M LiPF₆ in ethylene carbonate/Dimethyl carbonate (1:1) as electrolyte. For the half-cell tests lithium insertion into the working electrodes is referred to as “discharge” and extraction as “charge”. To evaluate electrochemical performance of the samples: galvanostatic charge–discharge curves, rate performance and galvanostatic cycling were examined in the voltage range of 1–3 V (vs. Li/Li⁺). The cyclic voltammogram (CV) tests of the samples were carried out in the voltage range of 0–3 V to examine the electrode reaction kinetics under the scan rate of 0.2 mV/s. Galvanostatic charge–discharge curves and cycling performance were also studied in the wide voltage range of 0–3 V for Li₄Ti₅O₁₂/Li₂TiO₃ composite electrode. Electrical impedance spectra (EIS) were measured by applying a sine wave with an amplitude of 5 mV over the frequencies of 1000 kHz to 0.01 Hz at open circuit voltage (OCV).

Results and discussions

Figure 1. XRD pattern of (a) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (b) Li_2TiO_3 and (c) $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite.

X-ray diffraction patterns of phase pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$, Li_2TiO_3 and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite are shown in **Figure 1**. Peaks of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ indicate well crystalline cubic spinel structure (Fd3m) that match with the JCPDS card No. 49-0207, phase-pure Li_2TiO_3 can be indexed to the monoclinic structure (space group C2/c) matching JCPDS card No. 033-0831, $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite shows polycrystalline phase of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Li_2TiO_3 with good crystallinity. Enlarged portion from 35° – 45° in the Inset (figure 1) clearly presents the peaks of both the phases in the composite. The content of Li_2TiO_3 in the composite is approximately 20 % based on the XRD analysis.

Figure 2. Scanning electron micrographs of (a) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (b) Li_2TiO_3 and (c) $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite.

SEM images of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, Li_2TiO_3 and composite $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ are shown in **Figure 2** (a), (b) and (c), respectively. Micrographs of pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Li_2TiO_3 exhibit particle size distribution of 0.5–1 μm and 0.2–0.3 μm , respectively. Though $\text{Li}_4\text{Ti}_5\text{O}_{12}$ calcined for 3 hours exhibited size of 0.2–0.3 μm (Figure S2, Supporting Information), but could not serve as a reference due to occurrence of multi-phases in the sample (Figure S1). It can be seen that $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite exhibits small particle size, narrow size distribution of 0.3–0.5 μm and less agglomeration as compared to pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sample which shows wide range of particle size. This may suggest that in composite $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ second phase contributes in preventing the particle aggregation and grain growth owing to the competitive crystallization between the two phases and steric hindrance effect.²⁷ However, long hours heating for phase-purity has also caused the growth of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ grains upto micron size. SEM images do not show any considerable difference in the morphologies of pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and in-situ $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite probably due to the same synthesis process.

Figure 3. Low magnification TEM images: (a, d), SAED: (b, e) and HR-TEM: (c, f) of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Li_2TiO_3 , respectively.

Low magnification (LM) TEM images show dense particles of pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (**Figure 3** (a)) with average particle size of 1 μm (0.5–1.5 μm) and relatively smaller grains of Li_2TiO_3 (Fig 3 (d)) having average size around 0.3 μm with a little agglomeration. The corresponding selected-area electron diffraction (SAED) patterns of the microstructures (Figure 3 (b), (e)) display spots of polycrystalline samples which is attributed to the diffraction of electron beam by fewer number of micron size particles. The larger the particle size the fewer the spots scanned by the beam. Indexed spots correspond to the lattice planes of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Li_2TiO_3 , respectively. High resolution (HR) TEM images of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (Figure 3 (b)) and Li_2TiO_3 (Figure 3 (e)) exhibit fringe spacing of 0.47 nm and 0.48 nm which match with the d-spacing of the maximum intensity planes i.e. (111) of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and (002) of Li_2TiO_3 , respectively.

Figure 4. Low magnification TEM images: (a, b), SAED: (c), and HR-TEM: (d, e) of $\text{Li}_2\text{TiO}_3/\text{Li}_4\text{Ti}_5\text{O}_{12}$ composite, respectively.

LM-TEM of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite in Figure 4 (a), (b) reveals well dispersed particles of 0.3–0.5 μm with an average grain size of 0.4 μm which confirms the SEM results. SAED pattern of the composite particles (figure 4 (c)) identifies dual-phase with Indexed spots corresponding to $(002)L_2$ and $(110)L_2$ planes indicating Li_2TiO_3 phase, whereas, $(004)L_4$, $(111)L_4$, $(311)L_4$ planes indicate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase. The glowing bright spots in SAED images exhibit highly crystallized phases. HRTEM images (Figure 4 (d), (e)) of the selected areas (marked A and B in figure (b)) of the composite particle confirm the presence of both $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Li_2TiO_3 phases with phase interfaces (marked red) within the grain (figure 4 (d)) as well as at the grain boundary (figure 4 (e)). Fringe spacing of 0.25 nm corresponds to (-131) plane of Li_2TiO_3 and 0.48 nm corresponds to (111) plane of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase. Therefore, dual phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Li_2TiO_3 composite grains possess large number of interfaces of both phase-phase and grain boundaries, which are significant for improvement of electrochemical performance.³¹

Figure 5. Initial charge-discharge curves of (a) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (b) Li_2TiO_3 and (c) $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite at current density of 0.2 C in voltage range of 1–3 V.

Figure 5 (a), (b) and (c) show the initial charge-discharge curves of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, Li_2TiO_3 and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$, respectively, in the voltage range of 1–3 V. The initial discharge capacity of phase-pure micron-size $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (Figure 5 (a)) is 158 mAh/g at current density of 0.2 C. For 0.3 micron Li_2TiO_3 particles the initial discharge capacity at current density of 0.2 C lies around 12–17 mAh/g in the first five discharge cycles (1st, 2nd, 5th cycle), indicating that Li_2TiO_3 is electrochemically inactive as reported by other groups.^{25,38} Composite $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ yields initial discharge capacity of 150 mAh/g in the 1st cycle which drops to 140 mAh/g and 135 mAh/g in the 2nd and 3rd cycles. The variation in the capacity during first 3 cycles may be attributed to the Li-ions storage at the electrode-electrolyte interface or carbon black (used as the electronic conductor during electrode preparation).^{39–40} For $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite flat plateaus in the voltage versus capacity curves (Figure 5 (a) and (c)) around 1.55V/1.6V and 1.55V/1.5V, respectively, correspond to discharge/charge processes based on Li-ions intercalation/de-intercalation into the respective crystal structures accompanied with $\text{Ti}^{4+}/\text{Ti}^{3+}$ redox reactions.^{41,42} Minor voltage difference (0.05 V) of the plateau voltages 1.6V/1.55V ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) and 1.55V/1.5V ($\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$) at 0.2 C indicates negligible electrochemical polarization of the electrodes during Li^+ insertion/extraction.^{24, 28} This indicates good rate capability of the materials and suggests that the rate capability of the two materials is comparable to each other.

Figure 6. (a, b): Rate performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite, respectively, (c, d): Cycling performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite, respectively, in voltage range of 1–3 V.

Figure 6 (a) and (b) show the rate performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite at different current densities in voltage range of 1–3 V. It is obvious from figure 6 (b) that the discharge capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ is a little lower than that of pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as Li_2TiO_3 does not show electrochemical activity in the composite. However, the difference between the capacity values is decreasing with increased current density. At current density of 0.2 C (35 mA/g) capacities of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ are 150 mAh/g and 135 mAh/g,

respectively, with a difference of 15 mAh/g, whereas, at higher current density of 5 C (875 mA/g) this difference drops to 5 mAh/g. This suggests that rate performance of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite is comparable to $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Moreover, the capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite sustains a significant value of 90 mAh/g even at high current density of 10 C (1.75 A/g). These trends confirm that $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite shows good rate capability at high current rates benefiting from the interfaces as reported by Wang et al.²⁵ It can be seen that the initial discharge capacity rapidly fluctuates from 150–135 mAh/g at 0.2 C (Figure 5 (c), 6 (b)) and 146–130 mAh/g at 0.5 C (Figure 6 (d)) during first 3 cycles of data collection, after which the capacity attains stable values. This fluctuating capacity may be ascribed to the contribution from Li-ions storage at the electrode-electrolyte interface or carbon black.³⁹⁻⁴⁰

Comparing the cycling performance of the electrochemically active samples, shown in figure 6 (c) and (d), it can be seen that the discharge-capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ decays from 158 mAh/g to 140 mAh/g at a current density of 0.2 C over 50 cycles, showing the capacity loss of 11.4 % (capacity retention ~ 88.6 %). For $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite stable capacity of 135 mAh/g recorded over initial 10 cycles at 0.2 C reproduced itself in the last five cycles (35th–40th) of rate performance curves (Figure 6 (b)) indicating no capacity fading at 0.2 C over 40 cycles. Cycling curve at high current density of 0.5 C (Figure 6 (d)) revealed capacity retention of 98.45 % with discharge-capacity variation from 130 mAh/g to 128 mAh/g over 50 cycles. It reveals that Li_2TiO_3 has contributed in stabilizing the cycling performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at current rates of 0.2 C and 0.5 C, which is urged for longer cycling life of batteries. In practical batteries using $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes electrolyte decomposition and formation of solid electrolyte interface (SEI) protective layers does not take place in the initial charge/discharge cycles of battery due to high operating voltage of 1.55 V. Instead, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ undergoes interfacial reactions with the electrolyte solvents at a slow rate during battery cycling tests and long term storage. These interfacial reactions between DEC solvent of electrolyte and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ form solid electrolyte interface (SEI) film by consuming Li and O ions from the outermost surface of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (111) plane forming TiO_2 . This SEI layer stops further reactivity and decay of electrochemically active material. Dual-phase $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite comprises lithium-rich structure whereby, consumption of Li and O ions for SEI formation is fulfilled from Li_2TiO_3 , protecting the structural stability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode.^{25,43} Some groups have made attempts to stabilize cathode materials by incorporating small amounts of Li_2TiO_3 in the composite structures.⁴⁴⁻⁴⁶

Figure 7. Cyclic voltamograms of (a) $\text{Li}_4\text{Ti}_5\text{O}_{12}$, (b) Li_2TiO_3 , and (c) $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite electrode in the voltage range of 0–3 V at a scan rate of 0.2 mV/s.

Cyclic voltamograms of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, Li_2TiO_3 and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ electrode were recorded during 1st and 5th cycles in a wide voltage range of 0.0–3.0 V at a scan rate of 0.2 mV/s to examine the electrochemical kinetics as shown in Figure 7. $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ (Figure 7(c)) shows two anodic current peaks at 1.51/1.25 V (1st/5th cycle) and 0.7–0 V indicating two potentials for lithium intercalation into the lattice sites of active crystals as predicted in the first principle studies.⁶ Sharp cathodic peaks around 1.75/1.72 V (1st/5th cycle) strongly indicate lithium extraction, corresponding to two different insertion mechanisms. The cathodic/anodic peaks of the composite closely match with the $\text{Ti}^{4+}/\text{Ti}^{3+}$ oxidation/reduction reaction peaks of pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (Figure. 7(a)) corresponding to Li^+ extraction/insertion during charge/discharge process.⁴⁷ In comparison, CV of Li_2TiO_3 shows minor anodic/cathodic peaks in 1.4–0 V range, indicating negligible electrochemical kinetics. The unusual rise in the 1st cycles of CV curves (Figure 7(a), (b)) may be due to the decomposition of SEI film formed at low voltage around 0 V. However, this behavior was not found in the 5th stable cycles. CV curves of the composite exhibited large polarization (0.54 V) in the 1st cycle which reduced to a minimal value (0.21 V) upto 5th cycle. The large polarization at the electrode surface in the 1st cycle is ascribed to the Li^+ ion storage at the electrode-electrolyte interface during initial charge-discharge process.^{24,40,39,48} However, weak polarization effect in the 5th cycle, indicates good rate capability of the electrode.²⁴ Note that polarization effects normally increase with increased current rates. Sharpness of the peaks indicates good electrochemical reaction kinetics of the electrodes which is attributed to good crystallinity of the materials.

To further check the electrode kinetics electrochemical impedance spectroscopy was employed. The Nyquist plots of Li_2TiO_3 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ electrodes obtained at OCV are shown in Figure S₃(a) (Supporting information) alongwith the equivalent circuit used for fitting of the results. Plots comprise depressed semi-circles from high to medium frequency which corresponds to the charge-transfer resistance (R_{ct}) at the electrode/electrolyte interface and a constant phase-angle element (CPE). Linear Warburg region (W) at low frequency reflects diffusion of Li ions into the bulk of the material. R_s in the equivalent circuit denotes the total

internal resistance including the resistance of electrical contacts, electrode/electrolyte interface and separator and corresponds to the intercept of the impedance curve on the real Z axis at high frequency.²⁴ As shown in Figure S3(a), Li_2TiO_3 exhibited large R_{ct} value of 157 Ω . R_{ct} of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ (123 Ω) was a little larger than that of pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (106 Ω). This is consistent with the rate performance of the samples (figures 6 (a), (b)), as the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite with electrochemically inactive Li_2TiO_3 yields a little lower capacity as compared to pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Moreover, EIS of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite was also measured when fully discharged to 0 V (lithium inserted) at high rate of 0.5 C which exhibited low R_{ct} of 83 Ω (Figure S3(b)). The Low R_{ct} (83 Ω) suggests that composite shows good rate capability at high current rates, benefiting from the grain boundaries and interfacial areas between the two phases. Interfaces are favorable for decreasing the charge transfer resistance through interfacial storage mechanism.^{25,30} Though interface effects are not prominent at low current rates as charge can be accommodated without needing interfacial areas but at high currents interfacial charge storage becomes prominent.

Figure 8. Initial charge-discharge curves of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ electrode in voltage range of 0–3 V (a) at current density of 2.85 C and (b) Cycling performance at current densities of 2.85 C over 25 cycles and 5.7 C over 75 cycles.

Moreover, $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ electrode was examined for charge-discharge in the cut off voltage of 0–3 V to study the possible electrochemical characteristics as shown in **Figure 8** (a, b). The behavior of the electrode is surprisingly different from that in the range of 1–3 V. At current rate of 2.85 C the initial discharge curves show a plateau/step (upto 37 mAh/g /13 mAh/g) at 1.25V/1.55V (1st cycle/5th, 6th, 10th cycle) and sloping from 1.25 V/1.55 V to 0 V. The plateau at 1.25/1.55 V corresponds to the typical insertion of Li-ions into the 16c sites of the crystal structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$.^{2,5} The high reversible capacity of 203 mAh/g (5th–10th cycle) at 2.85 C (Figure 8 (a)) suggests reversible intercalation/de-intercalation of more than 3 Li^+ ions into the active $\text{Li}_4\text{Ti}_5\text{O}_{12}$ occupying other available sites i.e. 8a, 8b, and 48f, besides 16c sites in the unit

cell. Sloping of discharge curves from 1.25V/1.55V (1st cycle/5th, 6th, 10th cycle) to 0 V, indicates that Li-ions undergoing electrochemical insertion into 8a, 8b or 48f sites have different energies as compared to the ions occupying 16c sites (plateau at 1.25V/1.55) as reported by first principle calculations of Zhong et al.⁶ Similar capacity contribution has also been reported by other groups for pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ discharged to 0 V.⁴⁸ However, it can be noticed that the charge curves in cut off voltage of 0–3 V (Figure 8 (a)) resemble the ones recorded in 1–3 V range (Figure 5 (c)). This exhibits un-interrupted extraction of Li-ions from the crystal structure irrespective of insertion sites.

Irreversible capacity loss of 70 mAh/g is observed in the 1st charge-discharge cycle (Figure 8 (a)) at 2.85 C as the discharge capacity (lithium intercalation) of 231 mAh/g bears corresponding charge capacity (lithium de-intercalation) of 161 mAh/g. This capacity loss in the initial cycles may be attributed to the formation of solid electrolyte interface film on the surface of the electrode below 1 V.⁴⁹ This capacity loss is observed only upto 4 consecutive cycles as shown in the cycling performance of the composite (Figure 8 (b)) recorded at 2.85 C upto 25 cycles. This suggests that once the SEI film is formed there is no such capacity loss between the respective discharge and charge capacities as evident from the initial charge-discharge curves (5th–10th cycle) and cycling performance (over 25 cycles). It reveals that the material can deliver the reversible capacity upto 203 mAh/g at 2.85 C when cycled in the voltage range of 0–3 V. Cycling the electrode at a high current rate of 5.7 C upto 75 cycles, showed a reversible capacity around 140 mAh/g. The rate capability is comparable to and cycling stability is better than that reported previously for pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at 0–3 V.^{50,48} Thus, the composite electrode exhibits superior rate performance and good capacity retention at high rates of 2.85 C and 5.7 C in the voltage range of 0–3 V. These results suggest that though Li_2TiO_3 did not show any electrochemical activity even at low voltage of 0–1.25/1.55V, yet it played a key role in stabilizing the cycling performance at high current rates.

■ CONCLUSION

Single-phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$, Li_2TiO_3 and dual-phase $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite anode materials were prepared by sol-gel method. Structure and morphology studies by XRD, SEM and TEM analysis revealed well crystalline structures of phase pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$, Li_2TiO_3 and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ with average particle size of 1 μm , 0.3 μm and 0.4 μm , respectively. The electrochemical characteristics indicate that the rate performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite at different current densities is comparable to $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Negligible discharge capacity of 12–17 mAh/g reveals that Li_2TiO_3 is electrochemically inactive. $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ shows good rate performance of 90 mAh/g at high current rate of 10 C in voltage range of 1–3 V, benefiting from increased grain boundaries and interfacial areas in the composite material. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ exhibits capacity retention of 88.6 % at 0.2 C over 50 cycles. Whereas, $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ shows no capacity fading at 0.2 C (40 cycles) and capacity retention of 98.45 % at 0.5 C over 50 cycles revealing highly stable cycling performance in voltage range of 1–3 V. CV curves of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ in cut off voltage of 0–3 V exhibit two anodic peaks at 1.51 V and 0.7–0 V indicating two modes of lithium intercalation into the lattice sites of active crystal. Sharp cathodic peak around 1.72 V indicates dominant lithium extraction, corresponding to two

different intercalation mechanisms. Moreover, the electrode delivers superior rate performance of 203 mAh/g at 2.85 C and 140 mAh/g at 5.7 C with good capacity retention over 100 cycles in 0–3 V scans.

The prominent feature of excellent long-term cycling stability of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ anode material upto high currents is attributed to: increased number of tiny reaction sites between the interfaces of the two phases and long term structural stability of the electrochemically active crystals of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, owing to protective SEI-film formation on the surface by consumption of Li and O ions of inactive Li-rich Li_2TiO_3 phase. Superior rate performance of the composite at high current rates results from enhanced insertion/extraction of Li-ions into other available sites i.e. 8a, 8b or 48f, in addition to 16c sites of active crystals, when the electrode is discharged down to 0 V.

■ ASSOCIATED CONTENT

Supporting Information

XRD of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder annealed at 800°C for 3 h., SEM image of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder annealed at 800°C for 3 h. Nyquist plots of Li_2TiO_3 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ electrodes at OCV with equivalent circuit and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_2\text{TiO}_3$ composite at OCV before discharge and after fully discharged at 0.5 C.

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