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Electrochemical Characteristics and Li$^+$ Ions Intercalation Kinetics of Dual-Phase Li$_4$Ti$_5$O$_{12}$/Li$_2$TiO$_3$ Composite in Voltage Range of 0–3 V

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**ABSTRACT:** Li$_4$Ti$_5$O$_{12}$, Li$_2$TiO$_3$ and dual-phase Li$_4$Ti$_5$O$_{12}$/Li$_2$TiO$_3$ composite were prepared by sol-gel method with average particle size of 1 µm, 0.3 µm and 0.4 µm, respectively. Though Li$_2$TiO$_3$ is electrochemically inactive, the rate capability of Li$_4$Ti$_5$O$_{12}$/Li$_2$TiO$_3$ is comparable to Li$_4$Ti$_5$O$_{12}$ at different current rates. Li$_4$Ti$_5$O$_{12}$/Li$_2$TiO$_3$ 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 Li$_4$Ti$_5$O$_{12}$ delivers capacity retention of 88.6 % at 0.2 C over 50 cycles, Li$_4$Ti$_5$O$_{12}$/Li$_2$TiO$_3$ 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 Li$_2$TiO$_3$ in preventing undesirable reaction of Li$_4$Ti$_5$O$_{12}$ with the electrolyte during cycling. CV curves of Li$_4$Ti$_5$O$_{12}$/Li$_2$TiO$_3$ 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. Li$_4$Ti$_5$O$_{12}$ 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 Li₄Ti₅O₁₂ chemically compatible with the electrolytes as solid electrolyte interface (SEI) films form while operating below 1 V.⁴

Li₄Ti₅O₁₂ has a stable [Li₃][Li₄Ti₅O₁₂][O₁₂] 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 Li₄Ti₅O₁₂ fully occupying the 16c sites, with theoretical capacity of 175 mA h g⁻¹, when discharged to 1 V.⁵ In Li-intercalated Li₄Ti₅O₁₂ 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, Li₇Ti₅O₁₂ represents a structure denoted as [Li₆][Li₄Ti₅O₁₂][O₁₂], 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 Li₇Ti₅O₁₂ by first principle calculations.⁶ The authors predicted that pristine Li₄Ti₅O₁₂ can bear the theoretical capacity of 262 mAh/g transforming to Li₈.₅Ti₅O₁₂ when discharged to 0 V. Lithiation of Li₄Ti₅O₁₂ to Li₈.₅Ti₅O₁₂ at 8a sites accompanies a small lattice expansion of about 0.4 % which makes the charging/discharging process reversible without distortion of the spinel [Li₄Ti₅O₁₂] 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 Li₄Ti₅O₁₂ to Li₇Ti₅O₁₂ and Li₇Ti₅O₁₂ to Li₈.₅Ti₅O₁₂ compositions, respectively.

Inspite of the promising features of Li₄Ti₅O₁₂ anodes, achieving high power density (high current rate capability) is still impeded by low lithium diffusion coefficient ~10⁻⁹ cm²/s⁷ and electrical conductivity ~ 10⁻⁹–0⁻⁷ 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 architectures, particle size reduction to nano-size, substituting suitable dopants like Mg, Zn, Al⁶⁻¹⁸ and making composites with conductive metals i.e. Li₄Ti₅O₁₂/Ag¹⁹, Li₄Ti₅O₁₂/Cu²⁰, Li₄Ti₅O₁₂/CNT²¹. Moreover, binary and multinary compounds (composites) based-anodes like Li₄Ti₅O₁₂/TiO₂/C/CNTs, N-doped carbon coated Li₄Ti₅O₁₂ and Graphite Carbon-Coated Li₄Ti₅O₁₂ 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 Li₄Ti₅O₁₂ 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, Li₄Ti₅O₁₂/TiO₂ composites have been extensively studied for electrochemical characteristics, yet Li₄Ti₅O₁₂-Li₄Ti₅O₁₂/²⁴ and Li₄Ti₅O₁₂/Li₂TiO₃²⁵ 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 Li$_4$Ti$_5$O$_{12}$/Li$_2$TiO$_3$ composite by solid state synthesis, owing to rich grain boundaries.

In the present work, we have synthesized pristine Li$_4$Ti$_5$O$_{12}$/Li$_2$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. Li$_4$Ti$_5$O$_{12}$/Li$_2$TiO$_3$ shows stable cycling performance in comparison with pure Li$_4$Ti$_5$O$_{12}$. Moreover, Li$_4$Ti$_5$O$_{12}$/Li$_2$TiO$_3$ composite has also been studied for electrochemical kinetics in voltage range of 0–3 V. Li$_4$Ti$_5$O$_{12}$/Li$_2$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$_2$TiO$_3$, Li$_4$Ti$_5$O$_{12}$ and Li$_4$Ti$_5$O$_{12}$/Li$_2$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$_2$TiO$_3$ and composite Li$_4$Ti$_5$O$_{12}$/Li$_2$TiO$_3$ were obtained at 800 °C for 3 hours. However Li$_4$Ti$_5$O$_{12}$ powder calcined for 3 hours contained impurity phases of both TiO$_2$ and Li$_2$TiO$_3$ as shown in the XRD pattern (Supporting information, Figure S1). Sintering the sample for 2 hours resulted into pure Li$_4$Ti$_5$O$_{12}$, which is attributed to the transformation of TiO$_2$ and Li$_2$TiO$_3$ impurities into the desired Li$_4$Ti$_5$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$_2$TiO$_3$, Li$_4$Ti$_5$O$_{12}$ and Li$_4$Ti$_5$O$_{12}$/Li$_2$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-6360A 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 Li$_4$Ti$_5$O$_{12}$/Li$_2$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 flouride (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) Li$_4$Ti$_5$O$_{12}$ (b) Li$_2$TiO$_3$ and (c) Li$_4$Ti$_5$O$_{12}$/ Li$_2$TiO$_3$ composite.

X-ray diffraction patterns of phase pure Li$_4$Ti$_5$O$_{12}$, Li$_2$TiO$_3$ and Li$_4$Ti$_5$O$_{12}$/Li$_2$TiO$_3$ composite are shown in Figure 1. Peaks of Li$_4$Ti$_5$O$_{12}$ indicate well crystalline cubic spinel structure (Fd3m) that match with the JCPDS card No. 49-0207, phase-pure Li$_2$TiO$_3$ can be indexed to the monoclinic structure (space group C2/c) matching JCPDS card No. 033-0831, Li$_4$Ti$_5$O$_{12}$/Li$_2$TiO$_3$ composite shows polycrystalline phase of Li$_4$Ti$_5$O$_{12}$ and Li$_2$TiO$_3$ 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$_2$TiO$_3$ in the composite is approximately 20 % based on the XRD analysis.

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

SEM images of Li$_4$Ti$_5$O$_{12}$, Li$_2$TiO$_3$ and composite Li$_4$Ti$_5$O$_{12}$/Li$_2$TiO$_3$ are shown in Figure 2 (a), (b) and (c), respectively. Micrographs of pure Li$_4$Ti$_5$O$_{12}$ and Li$_2$TiO$_3$ exhibit particle size distribution of 0.5–1 µm and 0.2–0.3 µm, respectively. Though Li$_4$Ti$_5$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 Li$_4$Ti$_5$O$_{12}$/Li$_2$TiO$_3$ composite exhibits small particle size, narrow size distribution of 0.3–0.5 µm and less agglomeration as compared to pure Li$_4$Ti$_5$O$_{12}$ sample which shows wide range of particle size. This may suggest that in composite Li$_4$Ti$_5$O$_{12}$/Li$_2$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. However, long hours heating for phase-purity has also caused the growth of Li$_4$Ti$_5$O$_{12}$ grains upto micron size. SEM images do not show any considerable difference in the morphologies of pure Li$_4$Ti$_5$O$_{12}$ and in-situ Li$_4$Ti$_5$O$_{12}$/Li$_2$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 Li$_4$Ti$_5$O$_{12}$ and Li$_2$TiO$_3$, respectively.

Low magnification (LM) TEM images show dense particles of pure Li$_4$Ti$_5$O$_{12}$ (Figure 3 (a)) with average particle size of 1 µm (0.5–1.5 µm) and relatively smaller grains of Li$_2$TiO$_3$ (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 Li$_4$Ti$_5$O$_{12}$ and Li$_2$TiO$_3$, respectively. High resolution (HR) TEM images of Li$_4$Ti$_5$O$_{12}$ (Figure 3 (b)) and Li$_2$TiO$_3$ (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 Li$_4$Ti$_5$O$_{12}$ and (002) of Li$_2$TiO$_3$, respectively.
Figure 4. Low magnification TEM images: (a, b), SAED: (c), and HR-TEM: (d, e) of Li$_2$TiO$_3$/Li$_4$Ti$_5$O$_{12}$ composite, respectively.

LM-TEM of Li$_4$Ti$_5$O$_{12}$/Li$_2$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$_2$TiO$_3$ phase, whereas, (004)L$_4$, (111)L$_4$, (311)L$_4$ planes indicate Li$_4$Ti$_5$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 Li$_4$Ti$_5$O$_{12}$ and Li$_2$TiO$_3$ 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$_2$TiO$_3$ and 0.48nm corresponds to (111) plane of Li$_4$Ti$_5$O$_{12}$ phase. Therefore, dual phase Li$_4$Ti$_5$O$_{12}$ and Li$_2$TiO$_3$ composite grains possess large number of interfaces of both phase-phase and grain boundaries, which are significant for improvement of electrochemical performance.\textsuperscript{31}
Figure 5. Initial charge-discharge curves of (a) Li$_4$Ti$_5$O$_{12}$ (b) Li$_2$TiO$_3$ and (c) Li$_4$Ti$_5$O$_{12}$/Li$_2$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 Li$_4$Ti$_5$O$_{12}$, Li$_2$TiO$_3$ and Li$_4$Ti$_5$O$_{12}$/Li$_2$TiO$_3$, respectively, in the voltage range of 1–3 V. The initial discharge capacity of phase-pure micron-size Li$_4$Ti$_5$O$_{12}$ (Figure 5 (a)) is 158 mAh/g at current density of 0.2 C. For 0.3 micron Li$_2$TiO$_3$ 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$_2$TiO$_3$ is electrochemically inactive as reported by other groups.$^{25,38}$ Composite Li$_4$Ti$_5$O$_{12}$/Li$_2$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 Li$_4$Ti$_5$O$_{12}$ and Li$_4$Ti$_5$O$_{12}$/Li$_2$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 Ti$^{4+}$/Ti$^{3+}$ redox reactions.$^{41,42}$ Minor voltage difference (0.05 V) of the plateau voltages 1.6V/1.55V (Li$_4$Ti$_5$O$_{12}$) and 1.55V/1.5V (Li$_4$Ti$_5$O$_{12}$/Li$_2$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 Li$_4$Ti$_5$O$_{12}$ and Li$_4$Ti$_5$O$_{12}$/Li$_2$TiO$_3$ composite, respectively, (c, d): Cycling performance of Li$_4$Ti$_5$O$_{12}$ and Li$_4$Ti$_5$O$_{12}$/Li$_2$TiO$_3$ composite, respectively, in voltage range of 1–3 V.

Figure 6 (a) and (b) show the rate performance of Li$_4$Ti$_5$O$_{12}$ and Li$_4$Ti$_5$O$_{12}$/Li$_2$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 Li$_4$Ti$_5$O$_{12}$/Li$_2$TiO$_3$ is a little lower than that of pure Li$_4$Ti$_5$O$_{12}$ as Li$_2$TiO$_3$ 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 Li$_4$Ti$_5$O$_{12}$ and Li$_4$Ti$_5$O$_{12}$/Li$_2$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 Li$_4$Ti$_5$O$_{12}$/Li$_2$TiO$_3$ composite is comparable to Li$_4$Ti$_5$O$_{12}$. Moreover, the capacity of Li$_4$Ti$_5$O$_{12}$/Li$_2$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 Li$_4$Ti$_5$O$_{12}$/Li$_2$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 Li$_4$Ti$_5$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 Li$_4$Ti$_5$O$_{12}$/Li$_2$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$_2$TiO$_3$ has contributed in stabilizing the cycling performance of Li$_4$Ti$_5$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 Li$_4$Ti$_5$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, Li$_4$Ti$_5$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 Li$_4$Ti$_5$O$_{12}$ form solid electrolyte interface (SEI) film by consuming Li and O ions from the outermost surface of Li$_4$Ti$_5$O$_{12}$ (111) plane forming TiO$_2$. This SEI layer stops further reactivity and decay of electrochemically active material. Dual-phase Li$_4$Ti$_5$O$_{12}$/Li$_2$TiO$_3$ composite comprises lithium-rich structure whereby, consumption of Li and O ions for SEI formation is fulfilled from Li$_2$TiO$_3$, protecting the structural stability of Li$_4$Ti$_5$O$_{12}$ anode.$^{25,43}$ Some groups have made attempts to stabilize cathode materials by incorporating small amounts of Li$_2$TiO$_3$ in the composite structures.$^{44-46}$
Cyclic voltamograms of Li$_4$Ti$_5$O$_{12}$, Li$_2$TiO$_3$, and Li$_4$Ti$_5$O$_{12}$/Li$_2$TiO$_3$ composite electrode in the voltage range of 0–3 V at a scan rate of 0.2 mV/s.

Cyclic voltamograms of Li$_4$Ti$_5$O$_{12}$, Li$_2$TiO$_3$ and Li$_4$Ti$_5$O$_{12}$/Li$_2$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. Li$_4$Ti$_5$O$_{12}$/Li$_2$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. 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 Ti$^{4+}$/Ti$^{3+}$ oxidation/reduction reaction peaks of pure Li$_4$Ti$_5$O$_{12}$ (Figure. 7(a)) corresponding to Li$^+$ extraction/insertion during charge/discharge process. In comparison, CV of Li$_2$TiO$_3$ 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. However, weak polarization effect in the 5th cycle, indicates good rate capability of the electrode. 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$_2$TiO$_3$, Li$_4$Ti$_5$O$_{12}$ and Li$_4$Ti$_5$O$_{12}$/Li$_2$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$_c$) 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.\textsuperscript{24} As shown in Figure S3(a), Li$_2$TiO$_3$ exhibited large R$_{ct}$ value of 157 $\Omega$. R$_{ct}$ of Li$_4$Ti$_5$O$_{12}$/Li$_2$TiO$_3$ (123$\Omega$) was a little larger than that of pure Li$_4$Ti$_5$O$_{12}$ (106 $\Omega$). This is consistent with the rate performance of the samples (figures 6 (a), (b)), as the Li$_4$Ti$_5$O$_{12}$/Li$_2$TiO$_3$ composite with electrochemically inactive Li$_2$TiO$_3$ yields a little lower capacity as compared to pure Li$_4$Ti$_5$O$_{12}$. Moreover, EIS of Li$_4$Ti$_5$O$_{12}$/Li$_2$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 $\Omega$ (Figure S3(b)). The Low R$_{ct}$ (83 $\Omega$) 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.\textsuperscript{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 Li$_4$Ti$_5$O$_{12}$/Li$_2$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, Li$_4$Ti$_5$O$_{12}$/Li$_2$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 Li$_4$Ti$_5$O$_{12}$.\textsuperscript{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 Li$_4$Ti$_5$O$_{12}$ occupying other available sites i.e. 8a, 8b, and 48f, besides 16c sites in the unit
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.\textsuperscript{6} Similar capacity contribution has also been reported by other groups for pristine Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} discharged to 0 V.\textsuperscript{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.\textsuperscript{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 Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} at 0−3 V.\textsuperscript{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\textsubscript{2}TiO\textsubscript{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.

\section*{CONCLUSION}

Single-phase Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}, Li\textsubscript{2}TiO\textsubscript{3} and dual-phase Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}/Li\textsubscript{2}TiO\textsubscript{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 Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}, Li\textsubscript{2}TiO\textsubscript{3} and Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}/Li\textsubscript{2}TiO\textsubscript{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 Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}/Li\textsubscript{2}TiO\textsubscript{3} composite at different current densities is comparable to Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}. Negligible discharge capacity of 12-17 mAh/g reveals that Li\textsubscript{2}TiO\textsubscript{3} is electrochemically inactive. Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}/Li\textsubscript{2}TiO\textsubscript{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. Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} exhibits capacity retention of 88.6 % at 0.2 C over 50 cycles. Whereas, Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}/Li\textsubscript{2}TiO\textsubscript{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 Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}/Li\textsubscript{2}TiO\textsubscript{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 Li$_4$Ti$_5$O$_{12}$/Li$_2$TiO$_3$ anode material up to 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 Li$_4$Ti$_5$O$_{12}$, owing to protective SEI-film formation on the surface by consumption of Li and O ions of inactive Li-rich Li$_2$TiO$_3$ 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 Li$_4$Ti$_5$O$_{12}$ powder annealed at 800°C for 3 h., SEM image of Li$_4$Ti$_5$O$_{12}$ powder annealed at 800°C for 3 h. Nyquist plots of Li$_2$TiO$_3$, Li$_4$Ti$_5$O$_{12}$ and Li$_4$Ti$_5$O$_{12}$/Li$_2$TiO$_3$ electrodes at OCV with equivalent circuit and Li$_4$Ti$_5$O$_{12}$/Li$_2$TiO$_3$ composite at OCV before discharge and after fully discharged at 0.5 C.

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