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Carbon coated nano-LiTi₂(PO₄)₃ electrode for non-aqueous hybrid supercapacitor

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Abstract

Pechini type polymerizable complex decomposition method is employed to prepare LiTi₂(PO₄)₃ at 1000 °C in air. High energy ball milling followed by carbon coating by the glucose-method yielded C-coated nano-LiTi₂(PO₄)₃ (LTP) with a crystallite size 80 (±5) nm. The phase is characterized by X-ray diffraction, Rietveld refinement, thermogravimetry, SEM, HR-TEM and Raman spectra. Lithium cycling properties of LTP show that 1.75 moles of Li (~121 mAh g⁻¹ at 15 mA g⁻¹ current) per formula unit can be reversibly cycled between 2-3.4 V vs. Li with 83% capacity retention after 70 cycles. Cyclic voltammograms (CV) reveal the two-phase reaction mechanism during Li insertion/extraction. Hybrid electrochemical supercapacitor (HEC) with LTP as negative electrode and activated carbon (AC) as positive electrode in the non-aqueous electrolyte is studied by CV at various scan rates and by galvanostatic cycling at various current rates up to 1000 cycles in the range 0 to 3 V. Results show that the HEC delivers a maximum energy density of 14 Wh kg⁻¹ and power density of 180 W kg⁻¹.

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Introduction

In recent years, lithium-ion hybrid capacitors (Li-HEC) or asymmetric supercapacitors are receiving attention since they combine the advantages of Li-ion batteries (LIB) in terms of deliverable energy density (Wh kg^{-1}) and those of electrochemical double layer capacitors (EDLC) in terms of deliverable power density (W kg^{-1}) [1-4]. Thus, the Li-HEC can satisfy the demands of the portable power sources for the electric vehicles (EV) and hybrid-EVs. Generally, the HEC configuration comprises Li-ion intercalating/de-intercalating type electrode and EDLC-forming counter electrode in aqueous or non-aqueous electrolyte. In the above, Li-ion intercalating electrode undergoes Faradaic reaction (as in LIBs) thereby providing sufficiently high energy density, whereas the EDLC component obeys non-Faradaic mechanism (as in symmetric supercapacitor) and consequently delivers high power to the system [1, 3].

Activated carbon (AC) has been the electrode of choice for supercapacitors based on EDLC because of the high specific surface area and lower cost in comparison to other materials, like, RuO_2 , carbon nanotubes, graphene etc. There are a few reports on the Li-HEC using aqueous electrolytes, but those with non-aqueous electrolytes are of great interest because they can operate at higher voltages (up to $\sim 4\text{V}$) and hence, can deliver high power density and high energy density.

Non-aqueous Li-HEC have been investigated using LIB-cathodes, like, LiMn_2O_4 , $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$, LiFePO_4 etc., as positive electrodes (and AC as the negative electrode) [5-11]. Similarly, a few titanium (Ti) containing binary and ternary oxides, $\text{TiO}_2\text{-B}$ [12], $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [13,

14], LiCrTiO_4 [15] and TiP_2O_7 [16] have been studied as negative electrode (anode) and AC as the positive electrode. Of these, the AC/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ system in LiPF_6 dissolved in ethylene carbonate/ diethyl carbonate showed very promising behavior by way of energy density of 10 Wh kg^{-1} and power density of 2 kW kg^{-1} [13]. Here, the anode participates in the Faradaic reaction (that is, Li- intercalation/de-intercalation) whereas the cathode (AC) participates in the non-Faradaic reaction (adsorption/de-sorption of PF_6^- ions).

Lithium titanium phosphate, $\text{LiTi}_2(\text{PO}_4)_3$ adopts the so-called NASICON-type (sodium superionic conductor) framework structure [17]. The structure of $\text{LiTi}_2(\text{PO}_4)_3$ is a three dimensional framework and allows numerous ionic substitution at various lattice sites. The framework is built of PO_4 tetrahedra linked by the corners of TiO_6 octahedral units. Each PO_4 tetrahedron is connected with four TiO_6 octahedral units and conversely, TiO_6 units are connected with six PO_4 tetrahedra. The interstitial cavities generated within the network are of two types known as M1 and M2 sites. The M1 cavity is situated between two TiO_6 octahedral units and it is coordinated with trigonal antiprism of oxygens and is occupied by Li-ion in $\text{LiTi}_2(\text{PO}_4)_3$. The M2 cavity comprises distorted eight fold coordination and surrounded by M1 interstitial voids. Initially, it was believed that Li ions occupy the M2 sites during insertion to form $\text{Li}_3\text{Ti}_2(\text{PO}_4)_3$ [17]. However, Aatiq *et al.*, [18] reported that in $\text{Li}_3\text{Ti}_2(\text{PO}_4)_3$ compound the three Li-ions occupy the two tetrahedral sites, M3 and M'3, within M2 cavity in the ratio of 2/3:1/3, respectively.

Luo *et al.* [19, 20] reported studies on the Li-HEC in aqueous electrolyte, 1 M Li_2SO_4 with $\text{LiTi}_2(\text{PO}_4)_3$ as the anode and either AC or MnO_2 as the cathode. In both cases, severe capacity-fading was observed, possibly due to poor compatibility of the anode in the aqueous electrolyte. It will be of interest to investigate the Li-HEC in non-aqueous electrolyte, and for

this purpose we have prepared nano-size carbon-coated $\text{LiTi}_2(\text{PO}_4)_3$ employing the Pechini-type polymerizable complex decomposition method, and after due characterization, examined the Li-cyclability vs. Li-metal up to 70 cycles, and the properties of the Li-HEC, AC/ $\text{LiTi}_2(\text{PO}_4)_3$ up to 1000 cycles. Results are reported here.

Experimental section

Pechini type polymerizable complex decomposition method described by Mariappan *et al.* [21] was employed to prepare the $\text{LiTi}_2(\text{PO}_4)_3$ nanoparticles. Stoichiometric amounts of Ti metal (STREM, USA), $\text{LiOH}\cdot\text{H}_2\text{O}$ (Fisher, 99.9%) and $\text{NH}_4\text{H}_2\text{PO}_4$ (Fisher, 99.9%) were used as starting materials. First, 0.96 g of Ti metal powder was dissolved in H_2O_2 (30%, Merck, Germany) and ammonia solution (25% Merck, Germany) in a 2:1 volume ratio. After the complete dissolution of Ti metal, citric acid (3.84 g, Aldrich, 99.5%) was added followed by the aqueous solution containing $\text{NH}_4\text{H}_2\text{PO}_4$ (3.45 g) and $\text{LiOH}\cdot\text{H}_2\text{O}$ (0.42 g) and stirred continuously to get the homogeneous solution. In this synthesis, the molar ratio between citric acid (CA) to Ti metal ratio was fixed to 1:1 and ethylene glycol (EG) to CA molar ratio also kept 1:1. To achieve polyesterification process of metal complex, EG (1.24 g) was drop wise added with constant stirring and temperature was gradually increased to 80 °C using a hot plate and maintained for about 2 h. After that, a further increase in temperature resulted in a polymeric gel. The above gel was pyrolyzed at 325 °C for 2 h in air to obtain black coloured precursor powder. The powder was then heated at 1000 °C for 24 h in air to achieve single phase $\text{LiTi}_2(\text{PO}_4)_3$. The powder was then, ball milled for 1 h to reduce the particle size using SPEX 8000D, USA ball miller, in which 50 ml capacity stainless steel (SS) vessel with 10 g of SS balls and 2 g of $\text{LiTi}_2(\text{PO}_4)_3$ powder was used. Carbon-coating of the ball milled powder was carried out by dispersing it in glucose (5 wt.%, 0.25 g) solution and stirred continuously on a hotplate to evaporate the water. The glucose

containing dried powder was heated at 800 °C for 2 h in flowing Ar-atmosphere in a tubular furnace (Carbolite, UK) to decompose the glucose and enable carbon coating on the surface of $\text{LiTi}_2(\text{PO}_4)_3$ particles.

The structural identification was carried out using X-ray diffractometer (Bruker AXS, D8 Advance) equipped with Cu $K\alpha$ radiation. The Rietveld refinement was conducted using Topas V3 software. Morphological features were analyzed using field emission scanning electron microscope (FE-SEM, JEOL JSM-7600F) and transmission electron microscope (TEM, JEOL 2100F). Thermogravimetric analysis was conducted using TA Instruments Q500 in the air atmosphere at the heating rate of 2 °C per min. The Brunauer-Emmett-Teller (BET) surface area was measured using Quantachrome (Nova 3200 e) Surface area & Pore size analyzer and Raman spectra were recorded using a micro-Raman spectrometer (Horiba-JY T64000) in a backscattering configuration with an excitation wavelength of 532 nm with a power of 1 mW. Backscattered signal was collected through a 50X objective with laser beam size $\sim 2\mu\text{m}$.

The electrochemical characterization was carried out using the two electrode CR 2016 coin-cell configuration. The test electrode was prepared by mixing 75 wt.% of active material ($\text{LiTi}_2(\text{PO}_4)_3$), 10 wt.% of conducting additive (super P carbon, BET surface area $230\text{ m}^2\text{ g}^{-1}$) and 15 wt.% of binder (Kynar 2801). The *N*-methyl pyrrolidinone was used as solvent to dissolve the binder to form slurry and resulting slurry was coated on to an Al foil (20 μm thickness) using doctor blade technique. The slurry coated-Al foil was dried in an oven at 100 °C, pressed between stainless steel twin rollers, and punched to form circular discs of 16 mm dia. The electrode discs were dried in a vacuum oven at 80 °C for 12 h to remove any residual solvent. The activated carbon (AC) (BET surface area $880\text{ m}^2\text{ g}^{-1}$, Norit, The Netherlands) electrode was prepared by mixing with 75 wt.% AC (9 mg), 12.5 wt.% super P carbon (1.5 mg) and 12.5 wt.%

binder (1.5 mg) (Teflonized Acetylene Black (TAB), Hohsen, Japan) using ethanol to form free standing film. The resulting film was pressed on to a 16 mm dia (plain wave) stainless steel mesh (0.25 mm thickness, Goodfellow, UK) using hydraulic press by applying a pressure of 6 tons. The half cells, Li/LiTi₂(PO₄)₃ and Li/AC were assembled using Li-metal foil (Kyokuto Metal Co., Japan; 0.59 mm thick). The electrodes in the test cells were separated by microporous glass fiber separator (Whatman, Cat. No. 1825 047, UK) and 1 M LiPF₆ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 volume, Merck, Selectipur LP40) was used as the electrolyte. The HEC was fabricated using AC as cathode and LiTi₂(PO₄)₃ as anode, after suitable mass balance of the active materials. The cyclic voltammetric studies on carbon-coated LiTi₂(PO₄)₃ were performed at slow scan rate of 0.1 mV s⁻¹ between 2–3.4 V, in which metallic Li serves as both counter and reference electrode using Solartron, 1470E and SI 1255B Impedance/gain-phase analyzer coupled with a potentiostat. The supercapacitive behaviour of HEC was examined using the above instrument at various scan rates (2 to 50 mV s⁻¹) between 0–3 V. Galvanostatic cycling profiles of the half-cells and HEC were recorded using Bitrode battery tester (SCN 12-4-5/18, USA) at ambient temperature.

Results and discussion

Structure and morphology

The as-prepared powder of LiTi₂(PO₄)₃ is white and well-crystalline. After high energy ball-milling and carbon-coating, it is greyish-black. The Pechini's method of polymeric complex decomposition ensures thorough atomic-scale mixing of metal ions and phosphate ions during complex formation, and subsequent calcinations in air ensured the decomposition of the volatile components and formation of the crystalline compound [21]. The powder X-ray diffraction

(XRD) pattern of carbon-coated and bare $\text{LiTi}_2(\text{PO}_4)_3$ are shown in Figure 1. The observed patterns are refined and indexed according to rhombohedral-hexagonal structure with $R\bar{3}c$ space group. The Rietveld refined XRD patterns clearly indicate the formation of phase pure structure without any impurity phases like, Li_3PO_4 and rutile- TiO_2 . The lattice parameter values of bare and carbon-coated $\text{LiTi}_2(\text{PO}_4)_3$ are given in Table 1 along with Rietveld refined parameters. These values agree well with literature values ($a= 8.512 \text{ \AA}$; $c= 20.878 \text{ \AA}$; JCPDS 35-0754) [21]. The average crystallite size is also calculated during refinement using Scherrer formula and found to be $115 (\pm 5) \text{ nm}$ and $81 (\pm 5) \text{ nm}$ for bare and carbon-coated $\text{LiTi}_2(\text{PO}_4)_3$ powders, respectively. The observed crystallite size value of the as-prepared compound is in good agreement ($\sim 110 \text{ nm}$) with Mariappan *et al.*, [21] who synthesized the compound at 1000°C using the CA to Ti metal ratio of 1:1. As expected, ball milled $\text{LiTi}_2(\text{PO}_4)_3$ powder have a lower crystallite size values.

Figure 2a and b show the SEM and TEM photographs of carbon-coated $\text{LiTi}_2(\text{PO}_4)_3$ particles and clearly reveal nano-size particles with the size of $80\text{-}90 \text{ nm}$ showing weak agglomerations and irregular in shape. Filament-like carbon-coating on the surface of the particles is also observed in Fig. 2b. The average thickness of carbon coating is $\sim 3 \text{ nm}$, as can be seen from the HR-TEM lattice image (Fig. 2 c). The inter-planer d -spacing of $5.98 \text{ \AA}$ agrees well with the hkl of (0 1 2) of the $\text{LiTi}_2(\text{PO}_4)_3$. The selected area electron diffraction (SAED) patterns are given as inset in Fig. 2c. The SAED pattern clearly shows the bright spots, and they are indexed based on the interplaner spacings and XRD pattern of $\text{LiTi}_2(\text{PO}_4)_3$.

In order to estimate the amount of carbon present in the material after coating, TGA analysis was conducted in air up to 600°C . The weight loss of 2.3% was observed in the range $350\text{--}500^\circ\text{C}$. The observed weight loss agrees well with the expected weight loss of 2% for the 5

wt.% glucose ($C_6H_{12}O_6 \rightarrow 6C + 6H_2O$) when calcined in Ar-atmosphere (Fig. 2d). To study the nature of carbon coating on the surface of nano- $LiTi_2(PO_4)_3$ particles, Raman spectrum was recorded for bare and carbon-coated $LiTi_2(PO_4)_3$ and are presented in Figure 3. An obvious difference between bare and carbon-coated $LiTi_2(PO_4)_3$ is seen. Both bare and carbon-coated $LiTi_2(PO_4)_3$ exhibited the characteristic bands at 138, 177, 239, 274, 311, 352, 432, 448, 969, 989, 1007 and 1094 (± 2) cm^{-1} . In the case of carbon-coated $LiTi_2(PO_4)_3$, Raman bands at 432 and 448 cm^{-1} are merged and appeared at 438 cm^{-1} . Similarly the bands at 969, 989 and 1007 cm^{-1} are merged and shown at 998 cm^{-1} and this may be attributed to the reduction of particle size during high energy ball milling. The observed Raman bands are consistent with the previous reports on $LiTi_2(PO_4)_3$ [22, 23]. In addition to the above characteristic bands, carbon-coated $LiTi_2(PO_4)_3$ clearly reveals the existence of carbon with its two characteristic bands at ~ 1600 and ~ 1340 cm^{-1} . The band at ~ 1600 cm^{-1} corresponds to the G band with optically allowed E_{2g} vibrations of the graphitic structure, whereas broad band (D) ~ 1340 cm^{-1} is related to the disordered carbon [24]. The peak intensity ratio of D and G bands (I_D/I_G) provides information about the degree of crystallinity of the carbon covered on the $LiTi_2(PO_4)_3$. In the present case, the I_D/I_G ratio is 0.98, which predominantly contains sp^2 type carbon and thereby possessing good electronic conductivity [25].

Li-cycling of $LiTi_2(PO_4)_3$

The electrochemical Li-cycling behaviour of bare- $LiTi_2(PO_4)_3$ as well as carbon-coated nano- $LiTi_2(PO_4)_3$ (LTP) were studied in half-cell configuration. Preliminary cyclic voltammetric (CV) studies on bare- $LiTi_2(PO_4)_3$ did not show well-defined Li-insertion and extraction potentials at 2.4 V vs. Li and 2.6 V vs. Li, respectively. This behaviour is mainly ascribed to the poor electronic conductivity of bare- $LiTi_2(PO_4)_3$ (4.4×10^{-8} S cm^{-1}) [26]. Hence, further studies

are not carried out on bare-LiTi₂(PO₄)₃ system. On the other hand carbon-coated nano-LiTi₂(PO₄)₃ exhibited well-defined oxidation and reduction curves and are given in Figure 4 in the potential range, 2-3.4 V *vs.* Li at the scan rate of 0.1 mV s⁻¹ up to 30 cycles. The cell, Li/LTP showed an open circuit voltage (OCV) of ~3 V and the cell is first discharged to insert the Li-ions (and electrons) into crystal lattice thereby reducing the valancy of Ti⁴⁺ to Ti³⁺. Theoretically, maximum of two Li-ions can be inserted into and extracted from LiTi₂(PO₄)₃.

The CV clearly show sharp reduction peaks at ~2.38 V (*vs.* Li) and oxidation peaks at ~2.6 V (*vs.* Li) and reveals two-phase reaction mechanism [17]. It is obvious to notice that, during cycling the area under the peak tends to decrease in both oxidation and reduction process with cycle number and it indicates slow capacity fading.

Galvanostatic studies of Li/LTP cell were conducted at two different currents at room temperature up to 70 cycles. Figure 5a shows the initial (first-cycle) discharge-charge curves between 2–3.4 V *vs.* Li at currents of 15 and 120 mA g⁻¹. Assuming 1 C=138 mA g⁻¹, these currents corresponds to current rates, 0.11 C and 0.87 C, respectively. The discharge-charge profiles clearly show the large and distinct voltage plateaus, which correspond to the two-phase reaction mechanism and coincide well with the CV data. The insertion of two moles of Li corresponds to the theoretical capacity of 138 mAh g⁻¹. The cell delivered the initial discharge capacities of 121 (1.75 moles of Li) and 113 mAh g⁻¹ (1.64 moles of Li) at 0.11 C and 0.87 C rates, respectively. The capacity *vs.* cycle number plots, presented in figure 5b, clearly show small capacity fading during cycling, which is in good agreement with the trend shown in CV

studies. At the 70th cycle, the cells retained 83 and 75% of their initial discharge capacities at 0.11 C and 0.87 C rates, respectively.

It is pertinent to compare the present study on LTP with the data reported in the literature. Several authors reported the electrochemical performance of Li/LiTi₂(PO₄)₃: Patoux and Masquelier [17] reported synthesis of LiTi₂(PO₄)₃ by solid state method and subsequent ball milling with carbon and the cell delivered discharge capacities of ~120 and ~95 mAh g⁻¹ at the first cycle and after 40 cycles, respectively when cycled between 2–3.4 V vs. Li at 0.1 C. This corresponds to capacity retention of 79 %. Kosova *et al.*, [27] reported the mechanical activation of source materials during the synthesis of LiTi₂(PO₄)₃ by solid state route at high temperature (1000 °C) and those cells exhibited discharge capacity of 105 mAh g⁻¹ at current density of 0.1 mA cm⁻² between 2–3.5 V vs. Li. Wessells *et al.*, [28] reported the performance of LiTi₂(PO₄)₃ synthesized by Pechini's method followed by 4 wt.% carbon-coating and observed an initial discharge capacity of 115 mAh g⁻¹ at 1 C rate between 2-3 V vs. Li. The cell showed the capacity retention of 70% after 160 cycles at room temperature. Synthesis of oxygen deficient LiTi₂(PO_{4-δ})₃ phase was reported by Luo *et al.*, [26] and such phase was prepared under N₂ heat treatment after the synthesis of native LiTi₂(PO₄)₃ compound. The above compound showed a discharge capacity of 118 mAh g⁻¹ at 0.2 C when cycled between 1.5–3.5 V vs. Li. At 1 C rate, the cells delivered discharge capacities of 93 and 81 mAh g⁻¹ for native and oxygen deficient phases of LiTi₂(PO₄)₃, respectively. Liu *et al.*, [29] reported the insertion of more than two Li-ions into LiTi₂(PO₄)₃ during the initial discharge and obtained a capacity of ~170 mAh g⁻¹ and consequently observed irreversible capacity loss during first charge about ~30 mAh g⁻¹ when cycled between 1.5–3 V vs. Li. Data for only four cycles was reported which showed capacity-fade during cycling. Thus, the presently observed reversible capacities agree with the reported

values. Nevertheless, the capacity-fading noted in the present study ($\sim 0.3 \text{ mAh g}^{-1}$ per cycle at 0.11 C and 0.87 C rates up to 70 cycles) and in all the literature reports may be due to the intrinsic nature of the material.

Li-cycling of Activated Carbon (AC)

In the present study, AC is used as the cathode (positive electrode) in the HEC configuration. The AC electrode in the charge/discharge process is concerned with the adsorption/desorption of PF_6^- anions on the surface. Thus, electrochemical profiles of AC vs. Li are required to balance the mass between two electrodes in HEC [30]. The test cell, Li/AC was fabricated with 1 M LiPF_6 in EC:DMC as the electrolyte and showed an OCV of $\sim 3.2 \text{ V}$. Considering the decomposition potential of the electrolyte, upper cut-off potential was restricted to 4.6 V vs. Li. The Li/AC cell was cycled between 3-4.6 V vs. Li at constant current of 120 mA g^{-1} and the voltage-capacity profiles are presented in Figure 6. The profiles are typical of capacitors and showed an initial discharge capacity of 37 mAh g^{-1} and the capacity is maintained at about 33 mAh g^{-1} up to 100 cycles. The Li/AC cell showed columbic efficiency over 99% except for the few initial cycles, which clearly indicates the adsorbed PF_6^- anions on the AC are completely desorbed during discharge.

It is worth to mention that, in a symmetric supercapacitor comprising two electrodes from the same material and having same mass, the applied voltage splits equally between two electrodes. However, if the two electrodes are different in nature and operate with a different mechanism as in an asymmetric configuration like HEC, the applied voltage will split depending on the capacitance of each electrode. In such a situation, capacitance of each electrode is related to the mass and the specific capacitance of the active material. In order to get the optimum cell

voltage in an asymmetric capacitor, a mass balance between the two electrodes is necessary. Hence, based on the electrochemical performance of Li/LTP and Li/AC cells at 120 mA g⁻¹ current (discharge capacity of 102 mAh g⁻¹ and 33 mAh g⁻¹ for the former and latter, respectively), the mass of active material cathode (AC) to anode (LTP) in the HEC is optimized and fixed at 3:1 ratio (12.7 mg:4.2 mg).

Cycling properties of AC/carbon-coated nano-LiTi₂(PO₄)₃ hybrid electrochemical capacitor (HEC)

Figure 7 shows the CVs of AC/LTP hybrid electrochemical capacitor (HEC) with 1 M LiPF₆ in EC:DMC as the electrolyte, between 0–3 V at various scan rates, 2 to 50 mV s⁻¹. An ideal supercapacitor will exhibit rectangular shape CV. Here, the CV of HEC are more or less rectangular in shape at lower scan rates (2, 5 and 10 mV s⁻¹). This confirms the supercapacitor behaviour of fabricated AC/LTP HEC. The specific capacitance (C_{HEC}) values of HEC are calculated using the relation, $C_{HEC} = (\int i \Delta t = q) / V.m$, where, Δt is the time (sec.), V is the potential difference (Volts), m is the mass of the active materials used in both electrodes (16.9 mg), q is the total charge (coulomb) obtained by integration of positive and negative sweep in CV [16]. The AC/LTP HEC delivered the specific capacitance of 35, 30, 26, 21 and 14 F g⁻¹ for 2, 5, 10, 20 and 50 mV s⁻¹ scan rates, respectively. It is obvious to notice that, an increasing sweep rate leads to a decrease in net charge under the curve which results in a decrease in specific capacitance. As expected, during higher scan rates electrochemical reaction takes place mainly at the surface of the Li-ion intercalating host (LTP) rather than in the bulk, and hence complete participation of active material is restricted which translates to a decrease in specific

capacitance values [16, 31]. Similarly, the counter electrode (AC) experiences poor adsorption of PF_6^- anions at higher scan rates.

Galvanostatic cycling of AC/LTP HEC was investigated between 0–3 V at 30 mA g^{-1} at room temperature and the profiles are shown in figure 8a. The HEC was initially discharged to insert Li-ions in to LTP lattice and subsequently charged to upper cut-off potential. The energy storage mechanism of the HEC can be described as follows: During discharge, Li-ions are intercalated in to the crystal lattice from the electrolyte solution and during charging Li-ions are released in to the electrolyte. At the same time, PF_6^- anions are adsorbed and desorbed on the counter electrode (AC) during discharge and charge, respectively. Figure 8b represents the cycling performance of AC/LTP HEC at constant current of 30 mA g^{-1} up to 1000 cycles. The cell discharge capacitance (C_{cell}) was calculated using the relation, $C_{\text{cell}} = (i.t / \Delta V)$ and the specific discharge capacitance, $C_{\text{SP.HEC}} = (4C_{\text{cell}} / m)$, where i is applied current (amp.), t is discharge time (sec.) and ΔV is the potential difference (volts) [16, 32]. The AC/LTP HEC delivered a $C_{\text{SP.HEC}}$ of 63 F g^{-1} at first cycle and tends to fade slowly during cycling up to 1000 cycles. The capacitance fading during cycling is because of inherent nature of the LTP particles. A similar kind of decreasing trend was also noticed in the aqueous hybrid supercapacitor systems, like $\text{LiTi}_2(\text{PO}_4)_3/\text{AC}$ and $\text{LiTi}_2(\text{PO}_4)_3/\text{MnO}_2$ in 1 M Li_2SO_4 electrolyte by Luo *et al.* [19, 20]. Values of $C_{\text{SP.HEC}}$ of 41 and 30 F g^{-1} are noted at the 500th and 1000th cycle, respectively.

The HEC was also cycled at various currents from 60 to 120 mA g^{-1} up to 250 cycles between 0–3 V. The plot of $C_{\text{SP.HEC}}$ vs. cycle number is shown in Fig. 9a. An increasing current leads to a decrease in the specific capacitance values. In addition, $C_{\text{SP.HEC}}$ values show a decrease with an increase in the cycle number which is similar to the behaviour at a current of 30 mA g^{-1}

in Fig. 8b. At high currents (90 and 120 mA g⁻¹), there is a competition between Li-intercalation in to the bulk of LTP and interfacial Li-storage on the surface of the LTP particles, in which latter phenomena dominates resulting in smaller but stable values of $C_{SP,HEC}$ as a function of the cycle number. The energy density (E_{SP}) and power density (P_{SP}) are calculated using the relations: $P_{SP} = (\Delta E \cdot i / m)$ and $E_{SP} = (P_{SP} \cdot t)$, where $\Delta E = (E_{max} + E_{min})/2$ and E_{max} and E_{min} are, respectively, the potential at the beginning of discharge and at the end of discharge [16, 20]. Since, the AC/LTP HEC is experiencing capacitance fade at currents 30 and 60 mA g⁻¹, the average time for first and last cycle values are taken for the calculation of energy density. The Ragone plot (E_{SP} vs. P_{SP}) is presented in Figure 9b. The AC/LTP HEC delivered the maximum energy and power densities of 14 Wh kg⁻¹ and 180 W kg⁻¹, respectively. The obtained values are comparable to the previously reported non-aqueous HECs based on Li-intercalating type electrodes. For example, AC/nano-TiP₂O₇ system exhibited 13 Wh kg⁻¹ and 371 W kg⁻¹ energy density and power density, respectively in the non-aqueous medium [16]. Wang *et al.*, [12] reported performance of carbon nanotube/TiO₂-(B) in 1 M LiPF₆ dissolved in EC/DMC/DEC (1:1:1 vol.) as electrolyte and reported an E_{SP} of 12.5 Wh kg⁻¹ and the P_{SP} of 1.3 kW kg⁻¹. A hybrid capacitor system consisting of the AC/nano-crystalline-Li₄Ti₅O₁₂ attached on carbon nanofibers system with 1.0 M LiPF₆ in EC/EMC/DMC (1:1:1 vol.) electrolyte gave an E_{SP} of 40 Wh L⁻¹ and a P_{SP} of 7.5 kW L⁻¹ [14].

Conclusions

The LiTi₂(PO₄)₃ nanoparticles were synthesized by Pechini-type polymerizable complex decomposition method at 1000 °C in air followed by high energy ball-milling. The obtained particles with a crystallite size of 80 (±5) nm were carbon coated by the glucose-method (2.3 wt% and ~3 nm thick). The carbon-coated nano-LiTi₂(PO₄)₃ (LTP) particles was characterized

by X-ray diffraction, Rietveld refinement, thermogravimetry, SEM, HR-TEM and Raman spectra. A two-phase reaction mechanism during Li-insertion at 2.38 V and extraction at 2.60 V vs. Li was observed by cyclic voltammetry. Galvanostatic cycling studies showed that 1.75 and 1.64 moles of Li can be reversibly cycled between 2-3.4 V vs. Li at 0.11 C and 0.87 C rates, respectively (1 C=138 mAh g⁻¹). Capacity fading occurs at both C-rates at ~0.3 mAh g⁻¹ per cycle up to 70 cycles. The hybrid electrochemical supercapacitor (HEC) comprising activated carbon (AC) as cathode (positive) and LTP as anode (negative) in the non-aqueous electrolyte exhibited good cycling profiles and delivered maximum energy and power densities of 14 Wh kg⁻¹ and 180 W kg⁻¹, respectively.

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Figure captions

- Figure 1: Powder X-ray diffraction pattern of (a) carbon-coated nano- $\text{LiTi}_2(\text{PO}_4)_3$ (LTP) and, (b) bare $\text{LiTi}_2(\text{PO}_4)_3$
- Figure 2: (a) SEM picture of carbon-coated nano- $\text{LiTi}_2(\text{PO}_4)_3$ (LTP) particles; scale bar-1 μm (b) HR-TEM picture of LTP; scale bar-100 nm, (c) HR-TEM lattice image. Inset shows the selected area electron diffraction (SAED) pattern. Integer values in parenthesis are (h k l) planes. (d) TGA curve of LTP recorded in air with the heating rate of 2 $^\circ\text{C}$ per min.
- Figure 3: Raman spectra for (a) bare $\text{LiTi}_2(\text{PO}_4)_3$ and (b) carbon-coated nano- $\text{LiTi}_2(\text{PO}_4)_3$.
- Figure 4: Cyclic voltammograms of carbon-coated nano- $\text{LiTi}_2(\text{PO}_4)_3$, cycled between 2–3.4 V at the slow scan rate of 0.1 mV s^{-1} . Li metal acts as both counter and reference electrode. Integer numbers indicate the cycle number.
- Figure 5: (a) First-cycle galvanostatic discharge-charge curves of Li/carbon-coated nano- $\text{LiTi}_2(\text{PO}_4)_3$ (LTP) cell between 2–3.4 V at 15 and 120 mA g^{-1} currents. (b) Plot of capacity vs. cycle number at 15 and 120 mA g^{-1} currents.
- Figure 6: (a) Galvanostatic cycling curves of Li/AC between 3–4.6 V at 120 mA g^{-1} current. The first and 100th cycle are shown. (b) Plot of capacity vs. cycle number.

Figure 7: (a) Cyclic voltammograms (CV) of the hybrid supercapacitor (HEC), AC (activated carbon)/carbon-coated nano- $\text{LiTi}_2(\text{PO}_4)_3$ (LTP) recorded between 0–3 V in non-aqueous electrolyte (1 M LiPF_6 in EC:DMC 1:1 vol.), at various sweep rates.

Figure 8: (a) Galvanostatic cycling curves of HEC, AC/carbon-coated nano- $\text{LiTi}_2(\text{PO}_4)_3$ (LTP) between 0–3 V at 30 mA g^{-1} current. (b) Plot of the specific discharge capacitance ($C_{SP,HEC}$) vs. cycle number.

Figure 9: (a) Plot of the specific discharge capacitance ($C_{SP,HEC}$) vs. cycle number of HEC, between 0–3 V at currents of 60, 90 and 120 mA g^{-1} . (b) Ragone plot (E_{SP} vs. P_{SP}) of the HEC, AC/carbon-coated nano- $\text{LiTi}_2(\text{PO}_4)_3$ (LTP).

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Table 1: Hexagonal lattice parameters and relevant data on the NASICON type $\text{LiTi}_2(\text{PO}_4)_3$

	Bare $\text{LiTi}_2(\text{PO}_4)_3$	Carbon-coated $\text{LiTi}_2(\text{PO}_4)_3$
Lattice parameters		
$a(\text{\AA})$	8.510	8.515 (8)
$c(\text{\AA})$	20.844 (3)	20.912 (7)
Crystallite size (± 5) (nm)	115	80
$R_{\text{wp}}\%$	8.2	7.7
$R_{\text{p}}\%$	5.9	5.3
GOF	6.8	6.4
$R_{\text{Bragg}}\%$	5.8	5.6
BET Surface area (± 0.2) ($\text{m}^2 \text{g}^{-1}$)	-	20