



Short communication

High-rate nano-crystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ attached on carbon nano-fibers for hybrid supercapacitors

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ABSTRACT

A lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$)-based electrode which can operate at unusually high current density (300 C) was developed as negative electrode for hybrid capacitors. The high-rate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode has a unique nano-structure consisting of unusually small nano-crystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (ca. 5–20 nm) grafted onto carbon nano-fiber anchors (nc- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNF). This nano-structured nc- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNF composite are prepared by simple sol–gel method under ultra-centrifugal force (65,000 N) followed by instantaneous annealing at 900 °C for 3 min. A model hybrid capacitor cell consisting of a negative nc- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNF composite electrode and a positive activated carbon electrode showed high energy density of 40 Wh L⁻¹ and high power density of 7.5 kW L⁻¹ comparable to conventional EDLCs.

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1. Introduction

EDLCs are energy storage devices that have excellent characteristics such as high safety, high power density (10^3 – 10^4 W kg⁻¹) and long cycle life (>100,000 cycles). [1–3] However, it is admitted EDLCs have limited energy density (10 Wh kg⁻¹), which restricts applications to power delivery over only several seconds [4]. In order to obtain higher energy density, many studies have been undertaken for the various hybrid capacitor systems, coupling redox-active materials (e.g., graphite, [5,6] metal oxides, [7–9] conducting polymers [10,11]) and activated carbon (AC). Recently, a new “lithium ion capacitor system” is attracting much attention, using a pre-lithiated (pre-doped with lithium ions) graphite as negative electrode with a positive AC electrode. [3] Devices with cell voltages as high as 3.8–4.3 V have been achieved with high energy densities (up to 25 Wh kg⁻¹) [12]. The possible disadvantage of the lithium ion capacitor system is related to the process of pre-lithiation of the graphite electrode, leading to serious problems of cost effectiveness and assurance quality control when they are mass-produced. In addition, although energy density improvement is achieved, the high working voltage causes an electrolyte decomposition problem [13]. This may bring about risks due to long-term stability and safety issues.

$\text{Li}_4\text{Ti}_5\text{O}_{12}$, as an engineering material for a hybrid capacitor system, inherently has several advantages, specifically in energy

density and safety as listed below: (1) high columbic efficiency (>95% at 1 C) very close to the theoretical capacity of 175 mAh g⁻¹ [14–16], (2) thermodynamically flat discharge profile at 1.55 V vs. Li/Li⁺ [15,17], (3) zero-strain insertion that provides little volume change during charge–discharge [14,15], (4) little electrolyte decomposition (little solid electrolyte interface and little gas evolution) [18] and (5) inexpensive raw material. However, the greatest problem of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is its low power characteristics that stem from inherent poor Li⁺ diffusion coefficient (<10⁻⁶ cm² s⁻¹) [19] and poor electronic conductivity (<10⁻¹³ S cm⁻¹) [20].

Cheng et al. [21] prepared nano-sized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles with diameter of 100 nm by molten salt process using LiCl as high temperature flux. The hybrid capacitor cell using the prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as the negative electrode showed capacity retention as high as 80% even at high-rate of 60 C. They suggested that nano-sizing of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particle promote shorter pathways for solid-state diffusion of Li ions and result in better rate capability. The result indicates that nano-sizing is effective method to overcome poor Li⁺ diffusion coefficient of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. We believe, however, that it is necessary to improve the poor electric conductivity of the nano-sized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for further enhancement of power characteristics.

In order to overcome the two problems of poor Li⁺ diffusion coefficient and poor electric conductivity at the same time, in this study, a novel nano-crystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nested and grafted onto carbon nano-fibers (nc- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNF) were prepared by a unique technique (UC method) of the mechano-chemical sol–gel reaction under ultra-centrifugal force field (65,000 N) [22], followed by an instantaneous heat-treatment under vacuum for very short duration (3 min). The power characteristics of the prepared composite

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(nc-Li₄Ti₅O₁₂/CNF) were investigated with a half-cell or a model cell of hybrid capacitor system.

2. Experimental

2.1. Preparation of the nc-Li₄Ti₅O₁₂/CNF composite

The detailed preparation procedures for the nc-Li₄Ti₅O₁₂/CNF composites are described below:

- Two kinds of solutions (solutions A and B) were prepared. 3.706 g of tetrabutyl titanate [Ti(OC₄H₉)₄] was dissolved in isopropyl alcohol (Solution A). 0.7185 g of lithium acetate was dissolved into the mixture solution of isopropyl alcohol, deionized water, and acetic acid (Solution B). For the solutions A and B, the molar ratio of Li: Ti was controlled as 1: 1. CNF were used as received from Mitsubishi material Corporation [23]. The CNF is tubular carbon fiber consisting of 10–20 graphene layers, that are synthesized by the decomposition of carbon-containing gases called as catalytic chemical vapor deposition method [24]. The diameter and specific surface area of the received CNF are 15–20 nm and 200 m² g⁻¹, respectively. Solution A, solution B and 1.0 g of CNF were mixed in the UC vessel where the weight ratio of the CNF to the Li₄Ti₅O₁₂ was controlled to be unity on the basis of dosed Ti alkoxide weight. Thereafter, 65,000 N of mechano-chemical agitation was applied to the whole mixture in the vessel for 5 min. After drying the resultant black gel at 80 °C for 17 h under vacuum, the precursor-LiTiO/CNF composites were obtained.
- The precursors of amorphous LiTiO/CNF composites were annealed to give the nano-crystalline composite in order to obtain a reversible Li⁺ insertion–deinsertion operation. The annealing was performed for a short duration of 3 min. at 900 °C under vacuum.

2.2. Physicochemical characterizations of the nc-Li₄Ti₅O₁₂/CNF composite

The detailed nano-structure of the composites, such as the particle size distribution of the nc-Li₄Ti₅O₁₂ and the graphene layer networks of CNF were observed by high-resolution transmission electron microscopy (HR-TEM Hitachi H9500 model). X-ray diffraction (XRD, Rigaku RAD-2B) was used to characterize the crystalline structure of the nc-Li₄Ti₅O₁₂ in the composites. In order to characterize the stoichiometry of the composites, thermal analysis was performed under air atmosphere using a thermogravimetry–differential thermal analyzer (TG/DTA, Seiko Instruments TG/DTA6300).

2.3. Electrochemical characterizations of nc-Li₄Ti₅O₁₂/CNF composites

The electrochemical characteristics were evaluated using (a) a half-cell (Li/(nc-Li₄Ti₅O₁₂/CNF)) and (b) a hybrid capacitor ((nc-Li₄Ti₅O₁₂/CNF composite)/AC) system.

2.3.1. (a) Half-cell Li/(nc-Li₄Ti₅O₁₂/CNF composites) system

The half-cell was assembled with a Li metal electrode, and a nc-Li₄Ti₅O₁₂/CNF electrode, using 2032 coin-type cell. The electrolyte was a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) containing 1.0 M lithium tetrafluoroborate (LiBF₄) as an electrolyte salt. The nc-Li₄Ti₅O₁₂/CNF electrode was prepared by mixing 80% of the composite and 20% of polyvinylidene difluoride (PVDF) in *N*-methyl pyrrolidone. The mixture was coated on a Cu foil (current collector) and dried at 150 °C under vacuum. The thickness

of the nc-Li₄Ti₅O₁₂/CNF electrode was ca. 20 μm corresponding to loading weight of ca. 1 mg. Charge–discharge tests were performed under CC-mode between 1.0 and 3.0 V vs. Li/Li⁺ at several current densities ranging from 0.175 to 52.5 A g⁻¹.

2.3.2. (b) Hybrid capacitor (nc-Li₄Ti₅O₁₂/CNF)/AC system

The hybrid capacitor cells were assembled with the nc-Li₄Ti₅O₁₂/CNF composite negative electrode, and AC positive electrode, using a laminate-type test cell (Nippon Chemi-Con level 3 standards). Commercial nano-porous carbon with specific surface area of 1358 m² g⁻¹ and peak pore size of 1.78 nm (RP-20, Kuraray Chemical Corp.) was used as the AC for the positive electrode [25]. The electrolyte was a 1.0 M LiPF₆ ethylene carbonate (EC)/ethyl methyl carbonate (EMC)/dimethyl carbonate (DMC) (1:1:1 in volume). The current collector and thickness for the nc-Li₄Ti₅O₁₂/CNF electrode was aluminum foil and ca. 60 μm, respectively. Every other condition was identical to that for the half-cell. Charge–discharge tests were performed under CC-mode between 1.5 and 3.0 V vs. Li/Li⁺ at several current densities ranging from 0.2 to 30 mA cm⁻². For comparison, we assembled a normal non-aqueous EDLC cell which consisted of an AC anode and AC cathode with PC solvent containing 1.0 M tetraethylammonium tetrafluoroborate (TEABF₄).

3. Results and discussion

3.1. Physical properties

XRD analysis was performed to confirm the formation of the nc-Li₄Ti₅O₁₂ and the presence of the CNF in the nc-Li₄Ti₅O₁₂/CNF composites. Fig. 1a shows the XRD patterns of the prepared nc-Li₄Ti₅O₁₂/CNF composite and pristine CNF. The composite has several sharp diffraction peaks at 2θ = 18°, 35°, 42°, 57°, and 63°. These peaks correspond to (1 1 1), (3 1 1), (4 0 0), (5 1 1), and (4 4 0) planes of a face-centered cubic spinel structure with *Fd3m* space group [14,15], respectively, indicative of the formation of crystalline Li₄Ti₅O₁₂. Annealing at 900 °C under vacuum for 3 min well crystallizes the Li₄Ti₅O₁₂ precursor. A broad peak at around 24.5° is observed which corresponds to the (0 0 2) plane of the pristine CNF. [24] This means that the CNF exists in the annealed composite and preserves its graphene layer structure similar to the pristine CNF. The fact that there are no other peaks observed corresponding to some possible impurities such as TiO₂, Li₂CO₃, and Li₂TiO₃ [26,27] suggests that the composite is composed of only two species, crystalline Li₄Ti₅O₁₂ and CNF.

Thermogravimetric (TG) measurement of the nc-Li₄Ti₅O₁₂/CNF composite was performed under air to estimate the residual weight ratio of the CNF. The obtained TG curve is shown in Fig. 1b. The weight loss at 400–600 °C resulted from the oxidative decomposition of the CNF, and exactly 50 wt% of the nc-Li₄Ti₅O₁₂ remained. The 50 wt% is well-consistent with the weight ratio of the Li₄Ti₅O₁₂ to the CNF calculated on the basis of dosed Ti alkoxide weight before UC method. This fact implies that sol–gel reaction in the UC method stoichiometrically proceeds, and the optimized (very short duration) annealing does not cause oxidative decomposition of the CNF. Such stoichiometric preparation processes (UC method and instantaneous annealing) are the important factors for cost effectiveness of capacitor production.

The nano-structures and crystallinity of nc-Li₄Ti₅O₁₂ and CNF in the composite is observed by HR-TEM (Fig. 2a and b). Fig. 2a shows a bird's eye view of a HR-TEM image of the nc-Li₄Ti₅O₁₂/CNF composite. The CNFs in the composite have tubular structure in a diameter of 15–20 nm identical to pristine CNF (Fig. 2c), indicating that the composite have meso-porous structure similar to the pristine CNFs. [24] The Li₄Ti₅O₁₂ particles have a diameter of ca.

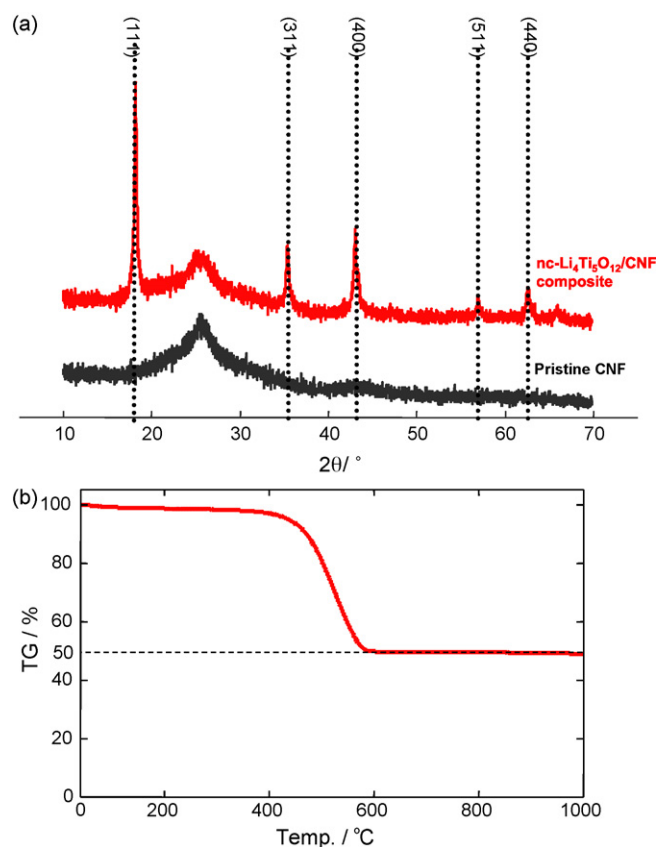


Fig. 1. Crystallinity and content of $\text{nc-Li}_4\text{Ti}_5\text{O}_{12}$ in the composite. (a) XRD patterns of the $\text{nc-Li}_4\text{Ti}_5\text{O}_{12}$ /CNF composite and pristine CNF. (b) TG curve of the $\text{nc-Li}_4\text{Ti}_5\text{O}_{12}$ /CNF composite at 1°C min^{-1} under air. The residual weight ratio corresponds to the content of $\text{nc-Li}_4\text{Ti}_5\text{O}_{12}$ in the composite.

5–20 nm and are well-dispersed among the CNFs. Moreover, all of the observed $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles are attached on the CNF surfaces. This results suggest that UC method induces to form and graft the nano- LiTiO precursors on CNF matrices as illustrated in Fig. 3. The subsequent instantaneous heat-treatment could achieve all of the following: (1) crystallization of the nano- LiTiO precursors, (2) inhibition of the CNF oxidation decomposition and (3) suppression of the agglomeration of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles.

In a worm's eye view of HR-TEM (Fig. 2b), the nano-sized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particle seems to be firmly tied on the CNF graphenes. Probably, the annealing at 900°C could lead to a formation of chemical bounds like an oxycarbide (Ti-O-C) at $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNF interface by carbothermal reduction reaction. [28] The fact that $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles can stably exist as small particles (5–20 nm) on CNF surfaces supports our speculation that chemical bounds were formed between $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and CNFs. The clear facet of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ reflects high crystallinity. This is consistent with the sharp XRD spectrum (Fig. 1a) despite such a nanosize. Such a high crystallinity resulted in a reversible and smooth Li^+ insertion performance. Also, HR-TEM images of CNF show clear graphene layers indicative of crystalline structure. Thus, this composite is considered to be the junction material of two crystalline species, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and CNF. This bound junction could bring about an establishment of good electronic paths between the two species.

3.2. Electrochemical properties

Fig. 4a shows the charge–discharge curve of the half-cell $\text{Li}/(\text{nc-Li}_4\text{Ti}_5\text{O}_{12}/\text{CNF})$ at 1C. The horizontal axis represents specific capacity per unit weight of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The dominant

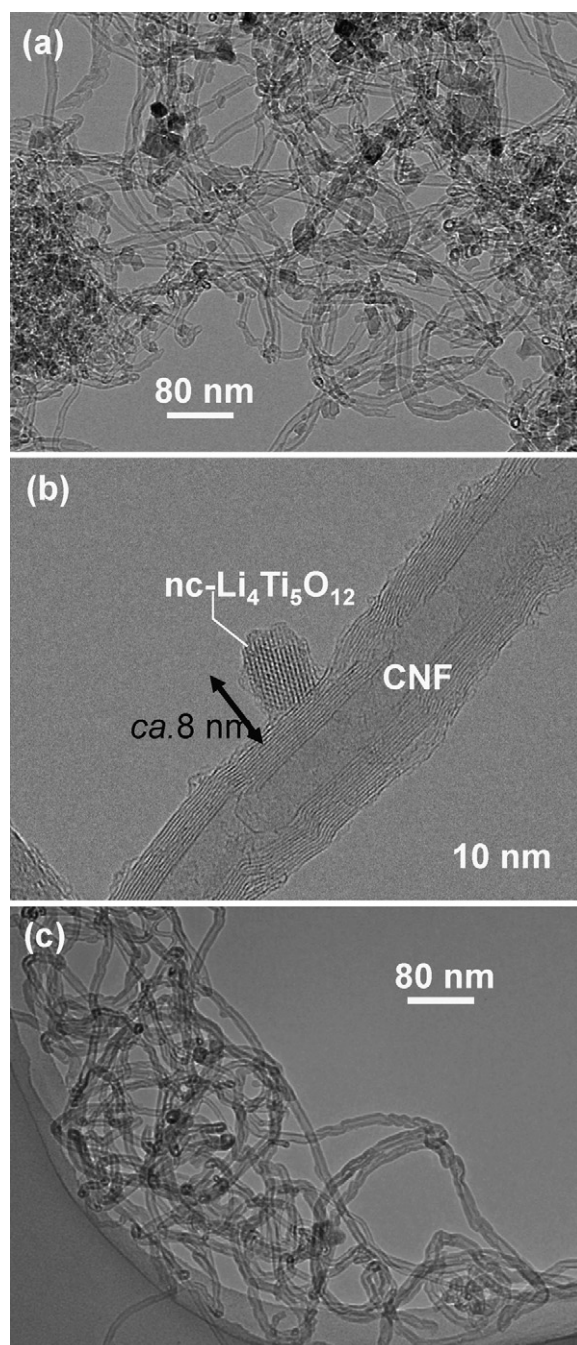


Fig. 2. Nano-structure of the $\text{nc-Li}_4\text{Ti}_5\text{O}_{12}$ and CNF. (a) A bird's eye view and (b) a worm's eye view of a HR-TEM image of the $\text{nc-Li}_4\text{Ti}_5\text{O}_{12}$ /CNF composite. (c) HR-TEM image of the pristine CNF.

plateau observed at ca. 1.5V vs. Li/Li^+ corresponds to the Li^+ intercalation–deintercalation process of the crystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [13,15], indicating that the capacity of the composite is determined by the redox capacity of $\text{nc-Li}_4\text{Ti}_5\text{O}_{12}$ in the composite. The obtained capacity was 167mAh g^{-1} per $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which is 95% of the theoretical capacity. It is noted here that the value of 167mAh g^{-1} is obtained after subtracting the double layer capacity of the CNF (8mAh g^{-1}). This result indicates that almost all of the $\text{nc-Li}_4\text{Ti}_5\text{O}_{12}$ particles in the composite are electrochemically active, meaning that ionic and electric paths are fully established in the composite. The rate capability of the obtained composite is shown in Fig. 4b. Even at a high rate of 300C, the composite shows reversible capacity of 158mAh g^{-1} per $\text{Li}_4\text{Ti}_5\text{O}_{12}$ which

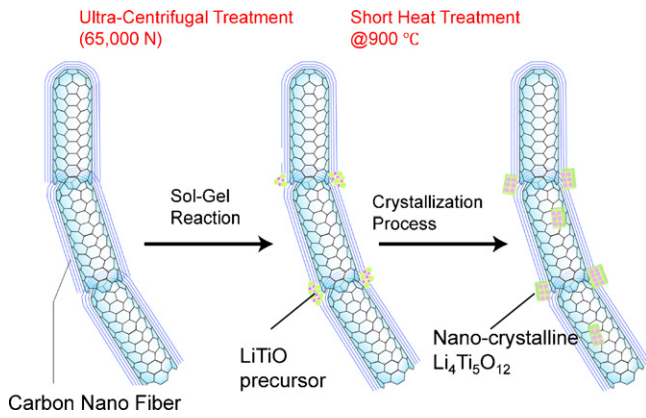


Fig. 3. Schematic illustration for the two-step formation procedure of the nc- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNF composite.

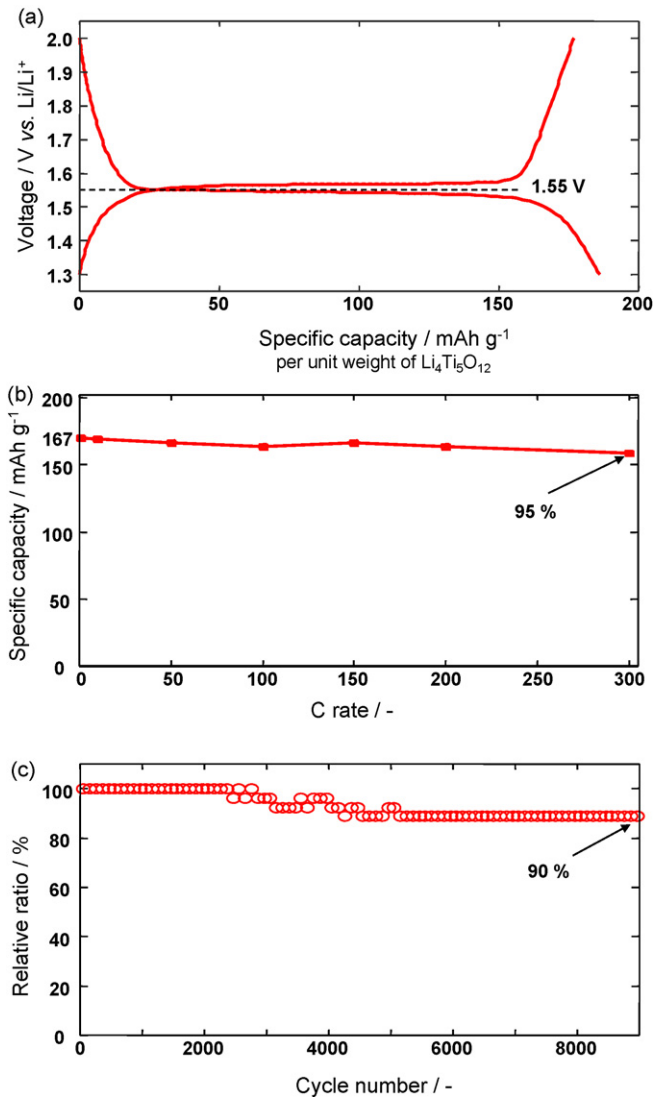


Fig. 4. Electrochemical properties of the nc- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNF composite. (a) Charge-discharge curve of nc- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNF composite between 1.0 and 3.0 V vs. Li/Li^+ at 1 C. (b) Rate capability of the nc- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNF composite in a C-rate range from 1 to 300 C. (c) Cycleability of nc- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNF composite between 1.0 and 3.0 V vs. Li/Li^+ at 20 C. 1 M $\text{LiBF}_4/\text{EC} + \text{DEC}(1:1)$ was used as the electrolyte for the all measurements.

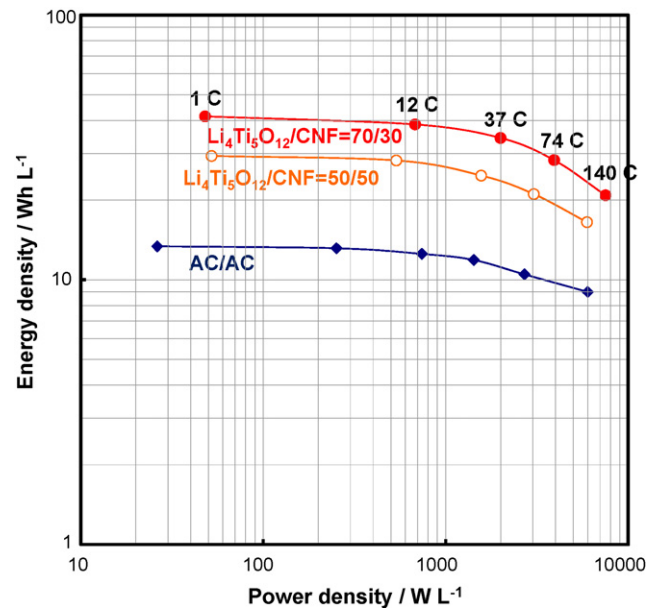


Fig. 5. Ragone plots of hybrid capacitor systems ((nc- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNF)/AC) and conventional EDLC system (AC/AC). The hybrid capacitor systems were assembled using two types of the composites with weight ratio of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNF = 50/50 or 70/30. The power and energy densities were calculated on the basis of the electrode volume.

correspond to 95% of the capacity obtained at 1 C. Such an excellent rate capability indicates that the optimized nano-structure of the nc- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNF composites as observed in HR-TEM image (Fig. 2) well overcome the inherent problems of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ materials like poor Li^+ diffusivity and poor electronic conductivity. Probably, this is because the nano-crystallized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNF junctions lead to facile ionic diffusion and electronic conduction, respectively. In conventional Li-ion batteries, such high-rate charge-discharge processes are known to cause significant heat generation leading to thermal runaway. However, W. Lu et al. [29] suggested that the heat generation rate of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ during charge-discharge is much smaller compared with that of graphite electrode for conventional Li-ion batteries because of its small entropy change. Therefore, this composite could be anticipated as high-rate electrode material not only for hybrid capacitors but also for Li-ion batteries. The cycleability of the composite is shown in Fig. 4c. Even after 9,000 cycles, 90% of the initial capacity is maintained, showing that the composite is electrochemically stable. The result strongly suggests that the aggregation and abrasion of the nc- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles hardly happen when they are operated at high-rate charge-discharge for a prolonged cycling.

Fig. 5 shows Ragone plots obtained from charge-discharge measurements for laminate-type cell of the hybrid capacitor system ((nc- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNF)/AC). Two types of composites with weight ratio of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNF = 50/50 or 70/30 were used as an active material for the hybrid capacitor system. The charge-discharge was performed between 1.5 and 3.0 V at various current densities ranging $0.2\text{--}30 \text{ mA cm}^{-2}$ ($0.18\text{--}26.8 \text{ A g}^{-1}$) corresponding to 1–140 C. For comparison, a conventional EDLC system (AC/TEABF₄-PC/AC) was also assembled and measured between 0 and 3.0 V. In a low power density range of $0.1\text{--}1 \text{ kW L}^{-1}$, the hybrid capacitor system based on the composite with weight ratio of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNF = 70/30 shows energy density as high as 40 Wh L^{-1} (55 Wh kg^{-1}), which is a value comparable to that of Li-ion capacitors [6]. Even at a high power of 7.5 kW L^{-1} , the energy density of the hybrid capacitor remains at 21 Wh L^{-1} which is double that of the conventional EDLC system (AC/AC). Comparing with similar hybrid capacitor cell consisting of nano-sized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles reported by Cheng et al.

[21], our hybrid capacitor cell shows higher power characteristics (55% of capacity at 1 C is maintained at 150 C). This result indicates that not only nano-sizing of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ but also establishment of electric paths plays important roles for enhancement of the power density. The results reveal that our capacitor system can provide higher energy as compared with conventional EDLCs not only in the low power density region ($0.1\text{--}1\text{ kW L}^{-1}$) but also in the high power density region ($1\text{--}6\text{ kW L}^{-1}$). Accordingly, this configuration of capacitor system is anticipated as an energy device utilizable for both high energy and high power applications.

4. Conclusion

In this study, we prepared a novel super-high-rate nano-crystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nested and grafted onto carbon nano-fibers (nc- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNF) by a unique technique (UC method) of mechano-chemical sol-gel reaction under ultra-centrifugal force field, followed by an instantaneous heat-treatment under vacuum for very short duration. The prepared nc- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNF well overcomes the inherent problems of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ materials like poor Li^+ diffusivity and poor electronic conductivity. A hybrid capacitor system consisting of the nc- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNF electrode and an AC electrode achieved high energy density of 40 Wh L^{-1} and high power density of 7.5 kW L^{-1} per electrode volume.

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