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Nano-Hybrid Capacitor Using Nano-$Li_4Ti_5O_{12}$/CNF Composites: High Energy Supercapacitors for Automotive Applications

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Abstract

Nano-hybrid capacitors having high energy density were developed by using a nano-sized $Li_4Ti_5O_{12}$/carbon nanofiber (CNF) composite as a negative electrode material. The $Li_4Ti_5O_{12}$ particles in the composite have diameters ranging from *ca.* 5 to 20 nm and are grafted onto the outer and inner surfaces of the CNFs. The nano-hybrid capacitor cell assembled with the nano-$Li_4Ti_5O_{12}$/CNF composite as a negative electrode and activated carbon as a positive electrode showed energy density of 36 Wh L^{-1}, which was almost three times as higher than conventional EDLC with similar high power densities. This high performance is attributed to the unique nano-structured $Li_4Ti_5O_{12}$/CNF composite which can overcome inherent problems of poor Li^+ diffusivity and low electric conductivity in $Li_4Ti_5O_{12}$ material. Furthermore, the nano-hybrid capacitor is much safer when compared with other high energy density hybrid capacitors such as Li ion capacitor (LIC). In cycle test at -10 ^oC, there was Li metal deposition was only observed in the LIC and not in the nano-hybrid capacitor. This result suggests that the nano-hybrid capacitor is much safer resulting from the nano-$Li_4Ti_5O_{12}$/CNF negative electrode operating at a potential of 1.55 V *vs.* Li/Li^+. Capability testing of the nano-hybrid capacitors at low temperatures showed *ca.* 80 % of capacitance retention at temperatures as low as -30 ^oC, which is drastically improved from *ca.* 50 % obtained by LIC. This excellent low temperature performance may be attributed to the low activation energy in electrochemical reaction due to nano-sizing of the $Li_4Ti_5O_{12}$.

Keywords: Hybrid capacitor, $Li_4Ti_5O_{12}$, Carbon nano-fiber, Nano-composite, Lithium ion capacitor

1 Introduction

Electric double layer capacitors (EDLCs) have the potential to emerge as a prominent energy storage technology due to their high energy density, power capability, and cycleability. One application of the EDLCs is as a secondary power system in heavy hybrid vehicles with stop-and-go driving such as city transit buses. The hybrid system can reduce fuel consumption and greenhouse gas emissions. However, this application requires the EDLCs to boost their energy density to downsize the power system.

Recently, Simon and Gogotsi [1] wrote a review article on EDLCs. This article highlights recent improvements in the energy of EDLCs were obtained by utilizing new approaches that increase their withstanding voltage. Developing new asymmetric (hybrid) capacitors is currently being investigated as an important alternative approach to achieving this same goal [2-5]. This approach can overcome the energy density limitations of conventional EDLCs because it employs a hybrid system using a battery-like (faradic) electrode and a capacitor-like (non-faradic) electrode, producing higher working voltage and capacitance.

One hybrid capacitor system called "Li ion capacitor (LIC)" that utilizes faradic charge storage has recently attracted the attention of many researchers [3, 4]. The LIC is a hybrid capacitor in which the positive and negative electrodes are made of activated carbon and graphite or hard carbon pre-doped with lithium ions, respectively. Since the negative electrode of graphite or hard carbon undergoes the reaction at a potential as low as 0 V *vs.* Li/Li^+, the LIC has a high working voltage of 3.8 V to 4.0 V. This high working voltage enables the LIC to realize both a high power density of approx. 5 kW kg^{-1} and an energy density of approx. 20 to 30 Wh kg^{-1}. The LIC thus exhibits favourable performance, and is regarded as a potential candidate of the next generation capacitor.

However, the LIC has potential disadvantages in regard to safety and reliability due to the low reaction potential of the graphite or hard carbon negative electrode. This has the potential of causing Li metal deposition, especially when operated at low temperatures. If deposition occurs a short circuit of the capacitor cell can result, which could cause the cell to explode or ignite. This disadvantage is likely a critical problem for automotive applications requiring rapid charging/discharging at low temperatures. Moreover, it is likely that the electrolyte solution may be decomposed at such a low potential, resulting in a premature degradation of capacitor performances.

In order to overcome these disadvantages and provide a safe and stable redox material, we have focused on lithium titanate ($Li_4Ti_5O_{12}$), which is capable of increasing the energy density of hybrid capacitors. The $Li_4Ti_5O_{12}$ functions as a redox material for our hybrid capacitors and provides the following critical advantages in energy density, stability and safety.

1) High columbic efficiency (>95%) [6-8]
2) Thermodynamically flat discharge profile at 1.55 V *vs.* Li/Li^+ [7, 9]
3) Zero-strain insertion that provide little volume change during charge-discharge [6, 7]
4) Minimal electrolyte decomposition [8]

A capacitor cell comprising $Li_4Ti_5O_{12}$ is, therefore, expected to provide unparalleled stability and safety. However, conventional $Li_4Ti_5O_{12}$ suffers from poor output power characteristics that stem from a low Li^+ diffusion coefficient (less than 10^{-6} cm^2 s^{-1}) [9] and a poor electronic conductivity (less than 10^{-13} S cm^{-1}) [10].

More recently, Prof. Naoi *et al.* were successful in overcoming these problems by nano-sizing the $Li_4Ti_5O_{12}$ particles and forming a composite with conductive carbon nano-fiber (CNF) [11]. The as-prepared nano-$Li_4Ti_5O_{12}$/CNF composite exhibited super-high-rate characteristics where 90% of the specific capacity obtained at 1C was retained when cycled at the extraordinary high rate of 300 C. In this study, we report the characteristics of the hybrid capacitor using the nano-$Li_4Ti_5O_{12}$/CNF composite as an active material for negative electrode.

2 Nano-structure of $Li_4Ti_5O_{12}$/CNF

Figure 1a is a bird's eye view of a TEM image of nano-$Li_4Ti_5O_{12}$/CNF composite prepared by our unique technique [11]. The TEM image shows granular substances are loaded on the tubular CNF surfaces which were not present on pristine CNF (Fig. 1c).

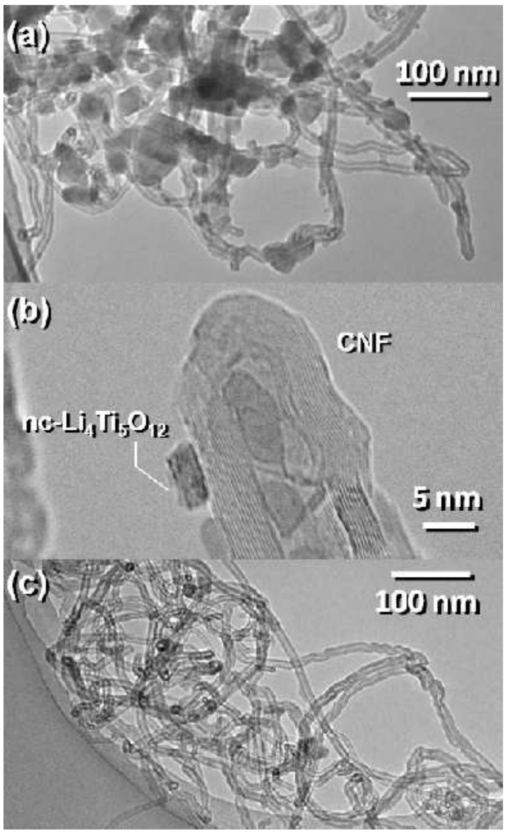

Figure1: TEM images of the $Li_4Ti_5O_{12}$/CNF (a and b) and pristine CNF (c).

The $Li_4Ti_5O_{12}$ particles obtained had considerably small diameters ranging from *ca.* 5 to 20 nm, and are highly dispersed. Moreover, all the observed particles are attached on the CNF suggesting that the nano-sized $Li_4Ti_5O_{12}$ particles are stabilized by attaching onto the surface of CNF.

In a magnified TEM image of the nano-composite (Fig. 1b), the $Li_4Ti_5O_{12}$ particles are observed to be attached not only on the outer surfaces but also on the inner surfaces of CNF. The clear facet of $Li_4Ti_5O_{12}$ makes it evident that the nano-crystals are highly crystalline which provides a structure capable of stable cycleability despite having nano-sized particles. The unique nano-structure of the nano-$Li_4Ti_5O_{12}$/CNF enables its high rate capability because of facile ionic and electric accessibility resulting from nano-sizing of $Li_4Ti_5O_{12}$ particles and electric pathways formed by conductive CNF, respectively.

3 Characteristics of a hybrid capacitor using $Li_4Ti_5O_{12}$/ CNF

The hybrid capacitor was assembled using the nano-$Li_4Ti_5O_{12}$/CNF composite as a negative electrode, activated carbon (AC) as a positive electrode, a propylene carbonate (PC) based non-aqueous electrolyte, and was finally sealed using a laminate-type test cell. The charge/discharge curve of the assembled test cell cycled between 1.4 and 3.0 V is seen in Fig. 2.

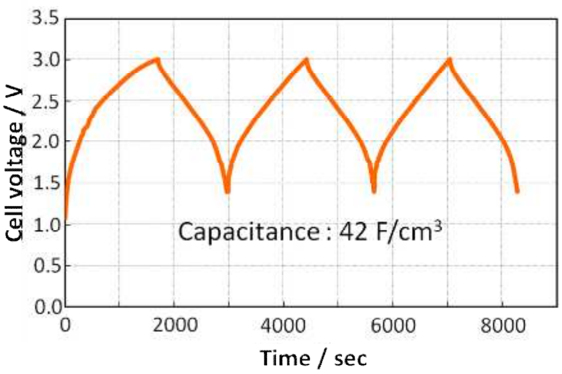

Figure 2: Charge-discharge curve of the hybrid capacitor cell using $Li_4Ti_5O_{12}$/CNF.

The hybrid capacitor exhibits a typical capacitive behaviour where the linear voltage rise results from the charging potential of the AC positive electrode during charging while the nano-$Li_4Ti_5O_{12}$/CNF negative electrode maintains a constant potential of 1.55 V *vs.* Li/Li^+. The potential of AC positive electrode reaches 4.35 and 4.55 V *vs.* Li/Li^+ at the cell voltage of 2.8 and 3.0 V, respectively. In practice the AC positive electrode in conventional EDLC is stable when operating at the potential of 4.35 V *vs.* Li/Li^+, which represents a operating and rated voltage of 2.5 V. Therefore the limitation of a cell voltage of the hybrid capacitor is considered to be 2.8 V, which corresponds to a capacitance of *ca.* 42 F cm^{-3} when normalized to the active material volume, and represents *ca.* 3.0 fold increase when compared with conventional EDLCs. The energy density (E) and the power density (P) of the hybrid capacitor cell were calculated from data of the charge/discharge measurements with various current densities using following equations (1) and (2)

$$E = \frac{V_1 \times V_2 \times C}{3600 \times L} \tag{1}$$

$$P = \frac{V_1 \times I}{L} \tag{2}$$

where the V_1, V_2 and I represent the average voltage, voltage change and a current during the charge/discharge measurement, respectively. The C and L are a capacitance and a volume of active material in the cell, respectively.

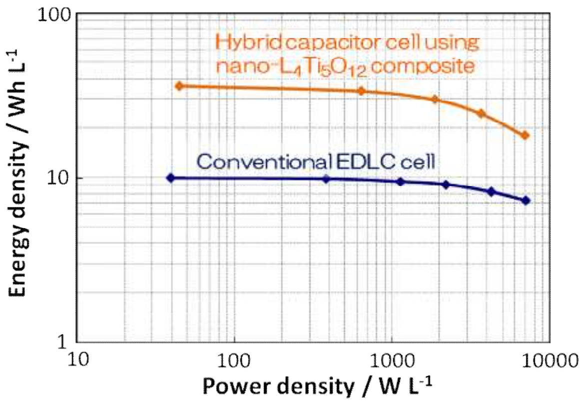

Figure 3: Ragone plots of the hybrid capacitor cell using $Li_4Ti_5O_{12}$/CNF and the conventional EDLC cell.

Ragone plots, normalized to the active material volume, are shown in Fig. 3 for the hybrid capacitor cell and a conventional EDLC cell made of activated carbon electrodes. When comparing these capacitors it can seen that the hybrid capacitor cell realized an energy density of 36 Wh L^{-1}, which was almost three times larger than the conventional EDLC cell, in the low power density range of 0.1 to 1 kW L^{-1}. Furthermore, even at a high power density of 6 kW L^{-1}, the hybrid capacitor cell exhibited an energy density of 18 Wh L^{-1}, which was 1.5 to 2.0 times higher than the energy density of the EDLC cell. It is evident that the hybrid capacitor using nano-$Li_4Ti_5O_{12}$/CNF composite can uniquely achieve a reliable and safe operation while providing both high energy and high power density.

In order to validate the safety of the nano-$Li_4Ti_5O_{12}$/CNF composite operation the electrode was monitored for Li deposition after cycling at low temperatures. No deposits were observed on the surfaces of the composite electrodes before or after 10,000 cycles between 2.0 and 1.0 V *vs.* Li/Li^+ at -10 ^oC as can be seen in the SEM images shown in Fig. 4a. The structure of the $Li_4Ti_5O_{12}$ composite electrode consisting of *ca.* 1-2 μm of particulate concavo-convex surfaces also remains unchanged after cycling. Also, the negative electrode consisting of hard carbon, used in LIC, was cycled between 0 and 1.5 V *vs.* Li/Li^+ at the same temperature of -10 ^oC. On the other hand, the hard carbon electrode did show deposited Li metal with localized concentrations on the electrode surfaces after 10,000 cycles as shown in Fig. 4b. This result verifies that Li deposition is unlikely for the nano-$Li_4Ti_5O_{12}$/CNF composite electrode while this still presents a problem for hard carbon electrodes, used in LIC. Thus, the hybrid capacitor using nano-$Li_4Ti_5O_{12}$/CNF can safely operate even in low temperature environments.

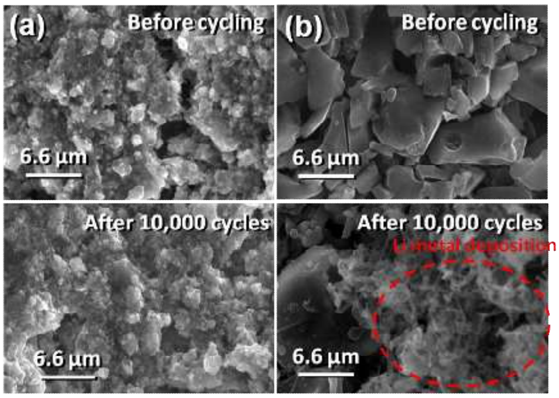

Figure 4: SEM images of $Li_4Ti_5O_{12}$/CNF electrode (a) and hard carbon electrode (b) after cycling at low temperature of -10 ^oC.

In addition to demonstrating exceptional safety the nano-hybrid capacitor showed outstanding stability. The results of DC loading test and cycle tests are shown in Fig. 5a and b, respectively. The hybrid capacitor cell is found to maintain *ca.* 90% of capacitance retention even after 1000 hrs at 2.8 V and 60 ^oC. This result suggests that the nano-$Li_4Ti_5O_{12}$/CNF composite is a stable redox material even at temperature as high as 60 ^oC, and is a suitable electrode material for the hybrid capacitors. The capacitance retention of the hybrid capacitor cell when cycled between 2.8 and 1.4 V kept a constant value of *ca.* 90% up to 15,000 cycles after a slight decrease in the capacitance during the initial few cycles as shown in Fig. 4b. This excellent stability is comparable to that of conventional EDLCs, and therefore the hybrid capacitor using nano-$Li_4Ti_5O_{12}$/CNF composite is anticipated to provide a long operational live capable of competing with EDLC energy storage devices.

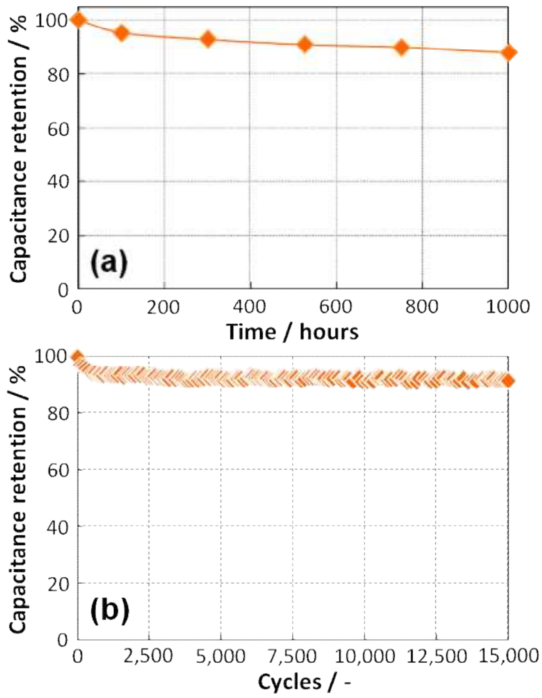

Figure 5: DC loading durability (a) and cycleability of the hybrid capacitor cell using $Li_4Ti_5O_{12}$/CNF.

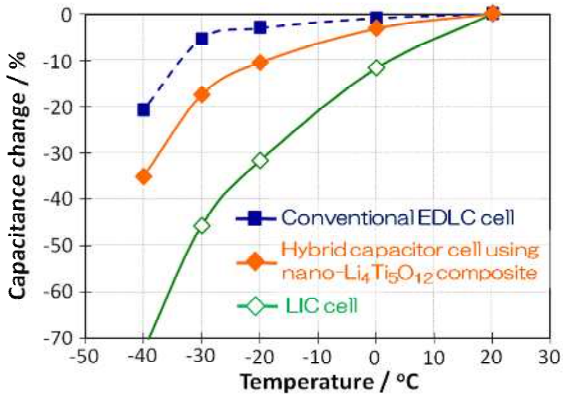

Figure 6: Capacitance change of the hybrid capacitor using Li4Ti5O12/CNF in a low temperature range of 20 to -40 ^oC.

Another advantage of the hybrid capacitor using nano-$Li_4Ti_5O_{12}$/CNF composite is a superior low temperature performance when compared with other competing hybrid capacitor technologies, such as LIC. Fig. 6 shows capacitance change of the hybrid capacitor cell comprising nano-$Li_4Ti_5O_{12}$/CNF composite, the normal EDLC cell and a normal LIC cell in a low temperature range of 20 to -40 ^oC. It is found that the hybrid capacitor cell using nano-$Li_4Ti_5O_{12}$/CNF composite exhibits very small capacitance change comparable to the EDLC cell in the low temperature rage, and the capacitance remains *ca.* 80% even at the temperature as low as -30 ^oC. In the case of LIC cell, on the other hand, the capacitance significantly decreases in the same low temperature range and reduced to *ca.* 50% at -30 ^oC. This excellent low temperature performance of the hybrid capacitor using nano-$Li_4Ti_5O_{12}$/CNF composite may be contributed to the reduced activation energy in electrochemical reaction by nano-sizing of $Li_4Ti_5O_{12}$ [12]. This result reveals that the hybrid capacitor using nano-$Li_4Ti_5O_{12}$/CNF composite has a desirable low temperature performance for automobile applications.

4 Conclusion

The unique nano-structure of the nano-$Li_4Ti_5O_{12}$/CNF composite allows it to overcome the inherent problems of $Li_4Ti_5O_{12}$ materials including poor Li^+ diffusivity and poor electronic conductivity making it the ideal material for hybrid capacitors. In fact, the use of the composite in the hybrid capacitor delivers *ca.* 3 times higher energy density while providing comparable power capability and reliability to the conventional EDLCs. Moreover, the hybrid capacitor using nano-$Li_4Ti_5O_{12}$/CNF composite have superior safety and low temperature performance when compared with other high-energy hybrid capacitors. Accordingly, the hybrid capacitor is expected to be a compelling next-generation capacitor for automotive applications as it fits all market requirements not only in term of energy and power, but also in safety and low temperature performance.

Acknowledgments

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