



Electrochemical Behavior of Lithium Titanium oxide/activated Carbon Composite for Electrochemical Capacitor

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ABSTRACT :

The $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite was prepared by sol-gel process with ultrasonication. The prepared composite was characterized by SEM, XRD and TG analysis, and their electrochemical behaviors were investigated by cyclic voltammetry, electrochemical impedance spectroscopy and charge-discharge test in 1 M LiBF_4/PC electrolyte. From the results, the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles coated on AC surface had an average particle size of 100 nm and showed spinel-framework structure. When the potential range of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite was extended from 0.1 to 2.5 V, redox peaks and electric double layer property were revealed. The initial discharge capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite was 218 mAh g^{-1} at 1 C. The enhancement of discharge capacity was attributed to electric double layer of added activated carbon.

Keywords : $\text{Li}_4\text{Ti}_5\text{O}_{12}$, activated carbon, electric double layer, electrochemical capacitor.

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1. Introduction

Electrochemical capacitors (ECs), also called supercapacitor, are electrochemical energy storage devices. The features of ECs are similar to those of electric double layer capacitor (EDLC) and rechargeable batteries. They may store charge in a Faradaic reaction as pseudocapacitance or may store charge in the double-layer of an electrode/electrolyte interphase.¹⁻⁴⁾ According to the charge storage mechanism, ECs are divided into electrochemical double layer capacitors (EDLCs) and pseudocapacitors. Recently, the electrochemical capacitors have been developed into an activated carbon electrode associated with a faradic electrode. The electrochemical capacitors normally consist of a double-layer capacitor electrode coupled with a battery electrode. For example, there are $\text{AC}/\text{Ni}(\text{OH})_2$ with an aqueous electrolyte or $\text{AC}/\text{Li}_4\text{Ti}_5\text{O}_{12}$ with a non-aqueous

electrolyte.⁵⁻⁸⁾ The improvement of the working voltage and energy density of the battery electrode material results in a significant increase of the overall energy density of the capacitors compared with that of EDLCs.⁹⁾

The electrochemical capacitors with activated carbon/graphite anode and nano-structured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ cathode have been developed in Li salt electrolyte.

These hybrid capacitors have some advantages over the traditional electric-double layer capacitors (EDLCs) in terms of high energy density.¹⁰⁻¹³⁾ But, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -based materials indicate intercalation-deintercalation which takes place at around 1.5 V vs. Li. So, the hybrid capacitor could be charged-discharged only between 1.2 and 3.2 V under the positive electrode. Therefore, another approach should be explored for extending the operating voltage of electrochemical capacitor. In this work, the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ deposited on activated carbon (AC) composite was prepared by sol-gel process with ultrasonication in order to extend the potential range of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ and further, its electrochemical behaviors have been investigated as anode electrode.

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2. Experimental

The $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite material was prepared by sol-gel process using the LiOH and tetra titanium isopropoxide (TTIP) with ultrasonication. Firstly, activated carbon (MSP-20, average particle size of $8\ \mu\text{m}$, $2190\ \text{m}^2\ \text{g}^{-1}$, Kuraray chem., Co., Ltd.) was stirred in 2-methoxy ethanol, and LiOH was dissolved in same solvent, respectively. After TTIP was dropped in LiOH solution, it was stirred for 2 hr in molar ratio of Li & Ti = 4.5 : 5. Then its solution was dropped in solution mixed AC. The mixed solution was performed by ultrasonication for 5 hr and separated from the solvent by drying at 110°C inside vacuum oven overnight. After the precursor was sintered at 850°C for 5 hr in Argon atmosphere, it was cooled to room temperature. Then navy gray powder of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite material was obtained.

The crystal structures of composite materials were characterized by X-ray diffraction using XDS 2000 (Sintag) model with $\text{Cu K}\alpha$ radiation source. The morphologies of composite materials were observed through a scanning electron microscopy (SEM, Hitachi S-2500C). Amount of carbon in composite materials was measured by thermo-gravimetry (TG) analysis with heating rate of $3^\circ\text{C}\ \text{min}^{-1}$ in air atmosphere from 30 to 900°C , by TA Instruments SDT2960.

The electrode was made of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ or $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite (80 wt%) as an active material, carbon black (10 wt%) as an electric conductor and CMC, SBR and PTFE (2 wt%, 4 wt% and 4 wt%) as a binder on a copper foil, respectively. Li disk was used as the counter and reference electrodes. Then this electrode was dried at vacuum at 120°C for 24 hr. It was fabricated for coin cell CR2016 model to measure electrochemical behaviors in 1 M LiBF_4/PC as electrolyte. And the electrochemical behaviors were investigated using cyclic voltammetry, AC impedance spectroscopy (Ivium stat) and charge-discharge test (Wonatech, WBCS3000).

The hybrid capacitor was made of activated carbon as cathode electrode and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite material as anode electrode with the same method above.

It was fabricated in 1 M LiBF_4/PC as electrolyte to coin type (CR2016) to measure electrochemical behaviors.

3. Results and Discussion

In order to show actual size and form of deposited $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particle, Fig. 1 presents SEM images of

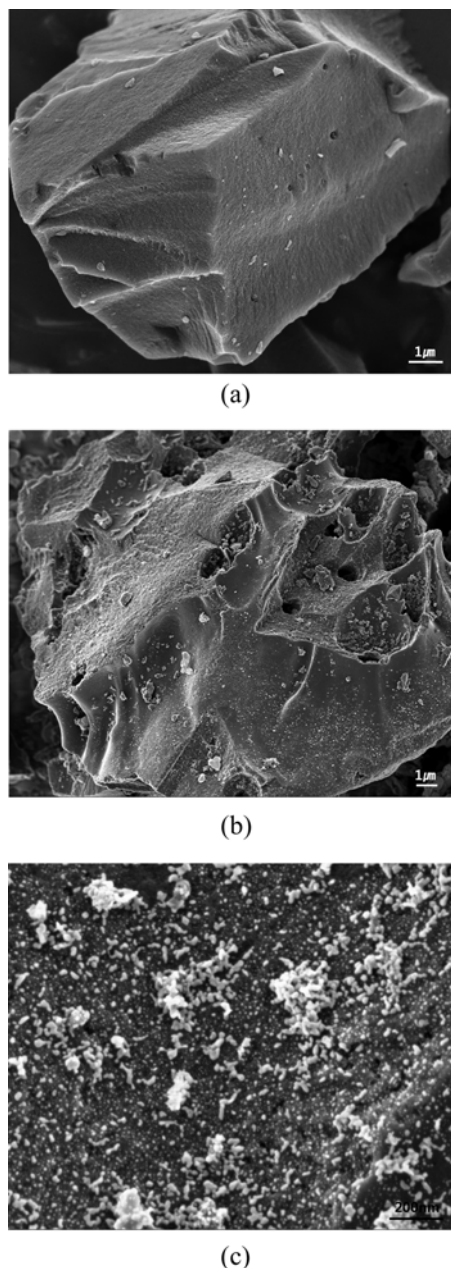


Fig. 1. SEM images of (a) the pristine AC, and (b), (c) $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite material.

$\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite materials. Fig. 1(a) shows the morphology of the precursor AC particles. As it shows, the precursor of AC particles had irregular size and shape of grains. The surface of AC particle is smooth and has also some carbon fragments adhering on. In contrast to the precursor, the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite materials have rough

vs. Li disk as a reference electrode. In the voltammograms of (a) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and (b) $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite electrode, redox peaks were observed in 1 M LiBF_4/PC electrolyte at a scan rate of 1 mV s^{-1} , respectively.

From the Fig. 4(a), there were a couple of peaks at 1.75 V/1.45 V with redox peaks of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, and peaks of under 0.7 V by $\text{Ti}^{3+}/\text{Ti}^{4+}$ side reaction. Any irreversible peak was not observed in the potential range of 0.7 to 2.5 V. The couple of peaks at 1.75 V/1.45 V could be attributed to the redox reaction of $\text{Ti}^{4+}/\text{Ti}^{3+}$, reaction mechanism of Eq. (1).¹⁴ In the voltammograms of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite electrode, the redox peaks in 1 M LiBF_4/PC electrolyte likely (a) $\text{Li}_4\text{Ti}_5\text{O}_{12}$. When $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles were deposited on AC particle, its current density was lower than pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particle as shown in Fig. 4(b). For amorphous AC particle, the redox peaks of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite electrode decreased.

A more detailed estimation about the electrochemical properties of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite electrodes can be carried out by the impedance spectra analysis. Fig. 5 shows Nyquist plots of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite electrodes in the frequency range 100 kHz to 10 mHz at the voltage of 0.3, 1.5, 1.6 and 2.2 V, respectively. The plot is composed of a semicircle at high frequency and an oblique straight line at low frequency. The semicircle reflects the electrochemical reaction resistance and the double layer capacity of the electrode. The resistance R_s , which corresponds to the electrolyte resistance, is similar at each voltage. However, the charge-transfer resistance

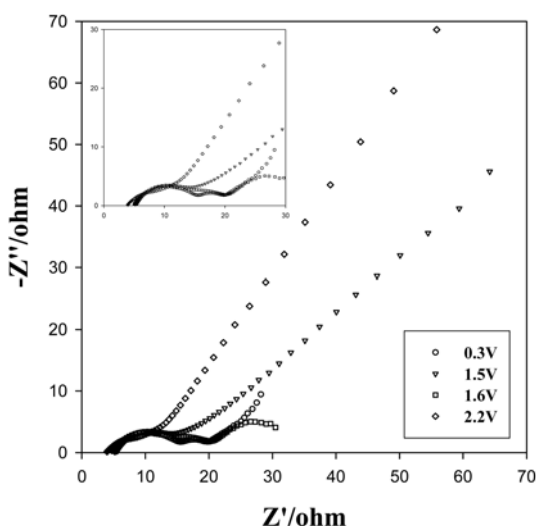


Fig. 5. Nyquist plots of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite electrode in LiBF_4/PC electrolyte. Frequency range : 100 kHz~10 mHz.

R_{ct} was increased at 0.3 and 1.6 V, respectively, resulting from electric double-layer and redox reaction with Li ion.

This result of Nyquist plot agreed well with that from the charge-discharge test. Fig. 6(a) shows the initial charge-discharge curves for the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite at a current density of 1 C at cut-off voltages 2.5-0.1 V. It clearly shows a curved line with 3 linear regions. The cell potential gradually increases up to 0.7 V (first step) during the first discharging and then suddenly increases up to 1.6 V. Next, it gradually increases up to 2.0 V (second step) for the insertion of lithium into $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and then suddenly increases up to 2.5 V (third step), for EDL. The each step of discharge capacities were 40, 160 and 18 mAh g^{-1} at 1 C, respectively. Second step discharge capacity is close the theoretical capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which is 175 mAh g^{-1} . Lithium insertion reaction follows next reaction:¹⁵⁾

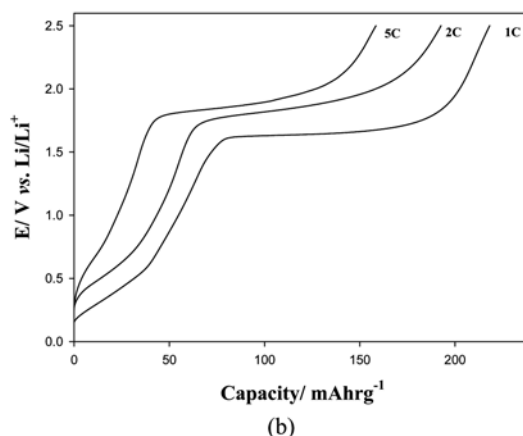
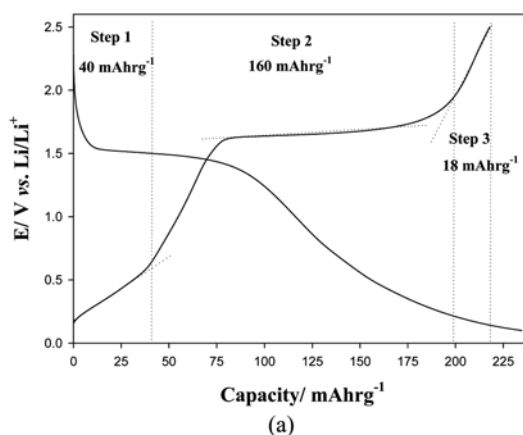
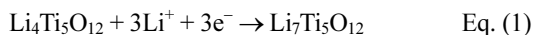


Fig. 6. (a) Charge and discharge behaviors of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite electrode at 1C. (b) Discharge profiles of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite electrode at 1 C and 5 C rates in LiBF_4/PC electrolyte.



Discharge capacity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite electrode was better than theoretical capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The discharge capacity enhanced by 20% was attributed to electric double layer of added activated carbon. This composite electrode has a high energy density because its working voltage is higher than the pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Fig. 6(b) shows the discharge curves of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite electrode at the current density of 1, 2 and 5 C, respectively. As the charge-discharge rate increase, the capacity decreases from 218 mAh g^{-1} (1 C) to 158 mAh g^{-1} (5 C). The discharge capacity at 5 C is 158 mAh g^{-1} , which is the 72% of discharge capacity at 1 C. When potential range is extended, discharge capacity of composite electrode was increased although the reversible discharge capacity was slightly decreased. These data show that the electrochemical behavior $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite electrode was improved and it is because of electric double layer of added activated carbon.

Fig. 7 shows the cycling behavior of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite electrode at different current value. Increasing discharge current, capacity of composite electrode was gradually decreased. The cycling stability may need to develop uniformed nano-size materials and improvement of preparation process with composite material.

Fig. 8 shows the discharge curves of hybrid capacitor. Discharge capacitance of hybrid capacitor was calculated with inside volume of coin cell (CR2016, 356 mm^3) of diameter 16 mm, height 1.4 mm at 1 mA cm^{-2} current value. This value was confirmed about 12 F L^{-1} . Discharge curves look like pseudo capacitance because of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ redox.

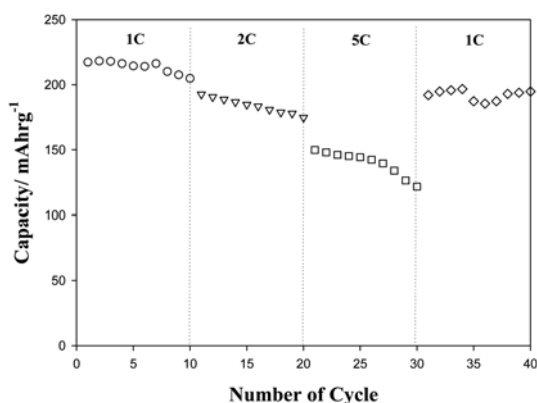


Fig. 7. Cycle life performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite electrode at 1 C and 5 C rates in LiBF_4/PC electrolyte.

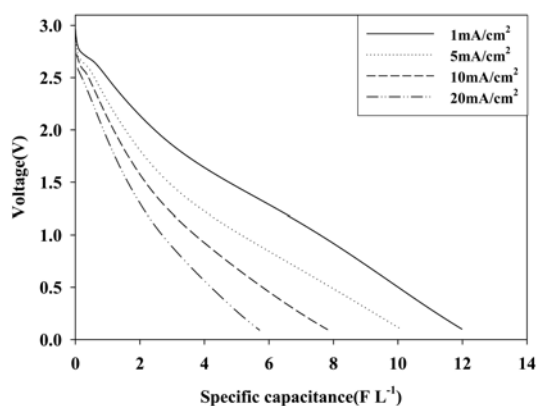


Fig. 8. Discharge behaviors of hybrid capacitor, using AC as cathode electrode, $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite electrode as anode electrode, series current value (1 mA cm^{-2} , 5 mA cm^{-2} , 10 mA cm^{-2} , 20 mA cm^{-2}) in LiBF_4/PC electrolyte.

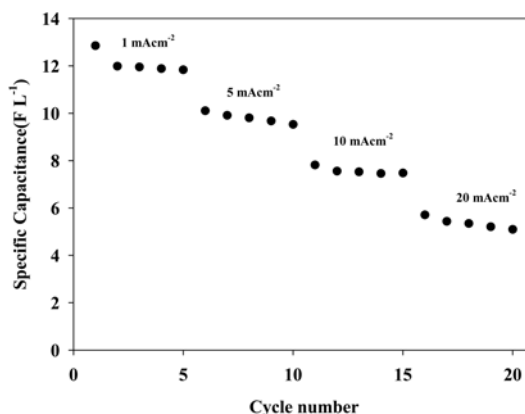


Fig. 9. Cycle life performance of hybrid capacitor, series current value (1 mAcm^{-2} , 5 mA cm^{-2} , 10 mA cm^{-2} , 20 mA cm^{-2}) in LiBF_4/PC electrolyte.

Fig. 9 shows the cycle life performance of hybrid capacitor. When current value increases, capacitance of hybrid capacitor decreases. Capacitance of hybrid capacitor decreases about one-half at 20 mA cm^{-2} than 1 mA cm^{-2} .

4. Conclusion

The $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite material was synthesized by a sol-gel method using ultrasound. $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite materials have an average size of 100 nm, spinel-framework structure for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles, and 42 wt% of AC contents. The improved electrochemical behavior of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ electrode was attributed to the addi-

tion of AC. When the potential range was extended 0.1 to 2.5 V, the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite observed redox peaks and electric double layer. The discharge capacity enhanced by 20% compared with pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at 1 C was attributed with electric double layer of added activated carbon.

However, compositing of carbon and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has disadvantage of closing up a pore of activated carbon with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and decreasing content ratio of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. And also, even though it is possible that hybrid capacitor operates in range from 0 V to 3 V through $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ composite material, we can not be sure of expanding potential only with this result.

Therefore, we need to conduct additional researches in interface of activated carbon and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ material, cycle life performance and generation of gas by decomposing of electrolyte.

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