

The Electric Properties of Surface Coating with CePO_4 and $\text{M}_3(\text{PO}_4)_2$ ($\text{M}=\text{Mg}, \text{Zn}$) on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for Energy Storage Capacitor

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Abstract – The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ of anode material for the hybrid capacitor was coated using CePO_4 , $\text{M}_3(\text{PO}_4)_2$ ($\text{M}=\text{Mg}, \text{Zn}$). The capacitance of phosphate coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was found to be lower than that of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, whereas the equivalent series resistance was higher than that of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. With an increase in cycle number, the base of cylindrical cell exhibited swelling due to gas generated from the reaction between $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and electrolyte. The swelling cycle number of phosphate coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was higher than that of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ due to improvement in electrochemical stability. Based on the results, it is proposed that phosphate coating can be employed as a barrier layer to control the gassing reaction by isolating the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particle from electrolyte solution.

Keywords: $\text{Li}_4\text{Ti}_5\text{O}_{12}$, surface coating, Hybrid capacitor, Gas generation

1. Introduction

Today, electro-chemical capacitors (ECs), also called as super capacitors, (electro-chemical double layer capacitor-EDLC), are in their process of emerging as a promising charge storage technology. They can complement or replace batteries employed for electrical energy storage and harvesting applications when high power delivery or uptake is necessitated [1-3]. ECs store electrical energy in the interface between an electrolyte and a solid electrode, thus forming an electric double layer. High surface area electrode materials, such as activated carbons, maximize this interface; resulting in generation of larger capacitance [4]. The weakness of ECs is the limited energy density, which restricts applications to power delivery of over only few seconds [5]. ECs, therefore present a new breed of technology, which occupies the niche amongst other energy storage technologies.

In order to meet these objectives, new electrode materials exhibiting high energy density are in demand. The spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) has been demonstrated as a potential candidate for the anode electrode material in high power Li-ion batteries as well as hybrid capacitors because of its good structure stability. LTO does not lead to any remarkably changes in the unit cell volume during the lithium ion insertion and extraction process [6]. The LTO inserts three lithium ions per formula unit, with a theoretical capacity of 175mAh/g, showing a voltage flat at 1.55 V versus a lithium electrode [7].

However, showed low intrinsic electronic conductivity and lithium-ion diffusion coefficient, resulting in poor high-rate charge/discharge capabilities. A number of strategies, including carbon coating, metal and non-metal

ion doping, hybridization with carbon and metal powders, reduction in particle size, and formation of micro-scale secondary particles consisting of nanostructure primary particles, have been devised to improve the electrochemical performance of LTO anode with varied success.

The disadvantage associated with LTO is gas severing during charge/discharge cycles and storage, especially at elevated temperatures. However, gassing in LTO-based LIBs is little understood although it leads to serious swelling and hence is of serious safety concern, and a main obstacle for widespread use of LTO-based batteries.⁸ Gassing behavior was generated by interfacial reaction between LTO and electrolyte solution. Therefore, in the present work, the effects of carbon coating on the electrochemical properties and gas generation of LTO were investigated.

2. Experimental Details

2.1 Synthesis and characterization of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and carbon coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$

The oxide powder of Li_2CO_3 (99%, Nippon chemical Industrial Co., Ltd, Japan) and TiO_2 (99.9%, Showa Titanium Co., Ltd, Japan) were employed as the starting materials. The powders were prepared according to the desired composition of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and ground with ZrO_2 balls for 24 h in ethanol. The mixed powder was calcined at 800°C for 6h to obtain a single phase.

To prepare the coating solution, $\text{M}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ ($\text{M}=\text{Ce}, \text{Mg}, \text{Zn}$) (99.9%, Aldrich, USA) and $(\text{NH}_4)_2\text{HPO}_4$ (99.9%, Aldrich, USA) were dissolved in distilled water, and the mixture was stirred with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for 1hr. The coating concentration was obtained as a 3wt% coating concentration. The coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was annealed at 700°C for 5h in air.

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Powder X-ray diffraction (Rigaku, Japan) analysis was used for phase identification. The X-ray diffraction data was measured in the 2θ range from 10° to 80° with a step size of 0.02° and a count time of 4s.

2.2. Preparation of electrode and cell assembly

The cathode of the hybrid capacitor was prepared by mixing activated carbon (BET: $\sim 2000\text{m}^2/\text{g}$, ash contents $< 400\text{ppm}$, average particle size $10\mu\text{m}$), conductive carbon black, and polytetrafluoroethylene (PTFE) as a binder in weight ratios 75:15:10. The anode electrode of the hybrid capacitor was prepared by mixing carbon-coated $Li_4Ti_5O_{12}$ powder, conductive carbon black (Super-P) and polyvinylidene fluoride (PVdF) as a binder with the weight ratios 87:7:6. N-Methyl-2-pyrrolidone (NMP) was used as a solvent. The slurry obtained from the mixture was coated by an aluminum current collector and dried at 150°C to remove the NMP solvent. The charge and discharge measurements were performed on a cylindrical cell (2245size). The hybrid capacitor cell was assembled using $Li_4Ti_5O_{12}$ and phosphate-coated $Li_4Ti_5O_{12}$ as an anode and activated carbon as cathode. The electrolyte was a 1.5 M solution of $LiBF_4$ and nonwoven fabric was used as the separator. The electrochemical performance was evaluated using a programmable multichannel battery tester (Arbin Instruments).

3. Results and Discussion

Fig. 1 shows the XRD patterns of LTO and surface coated LTO specimens using $CePO_4$, $M_3(PO_4)_2$ ($M=Mg, Zn$), (C-LTO, M-LTO, Z-LTO). A single phase with a spinel structure was detected through the entire range of compositions, which was confirmed based on all the peaks of the JCPDS file no. 49-02079 [9].

The SEM micrographs of LTO and surface coated LTO are shown figure 2. The average particle size of LTO and

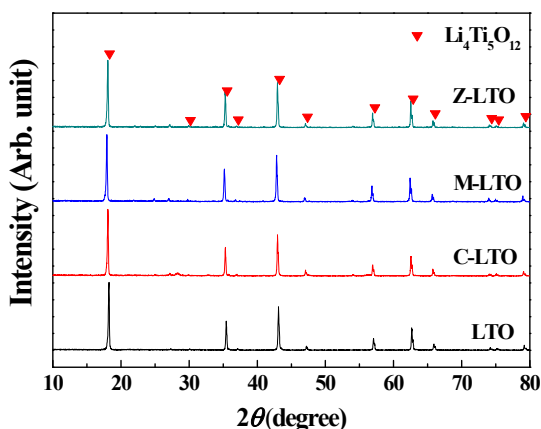


Fig. 1. The X-ray diffraction patterns of $Li_4Ti_5O_{12}$ and surface coated $Li_4Ti_5O_{12}$

surface coated LTO was 170-300nm in diameter. The particle size of LTO and surface coated LTO exhibited remarkable changes based on employment of different coating materials, because the annealing temperature was lower than calcined temperature of LTO.

Fig. 3 shows the capacitance and equivalent series

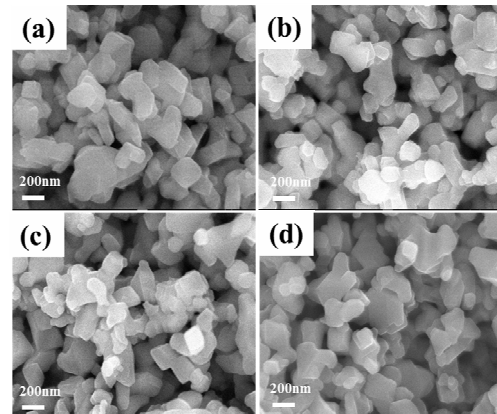


Fig. 2. The SEM micrographs of $Li_4Ti_5O_{12}$ and surface coated $Li_4Ti_5O_{12}$ ((a) $Li_4Ti_5O_{12}$, (b) C-LTO, (c) M-LTO, (d) Z-LTO)

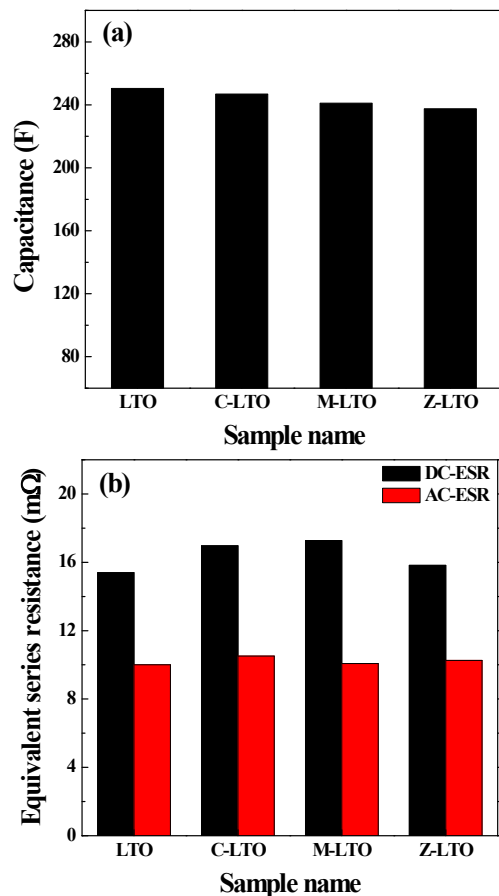


Fig. 3. The (a) capacitance and (b) equivalent series resistance of the hybrid capacitor prepared by employing different coating materials

resistance (ESR) of the hybrid capacitor with LTO and surface coated LTO. The capacitance of surface coated LTO was slightly decreased and AC/DC-ESR of surface coated LTO was slightly increased than those of LTO. The reaction region of lithium-ion intercalation and extraction was decreased by surface coating.

Fig. 4 shows the discharge capacity and DC-ESR retention of hybrid capacitor as a function of different coating materials at different charge/discharge current rates.

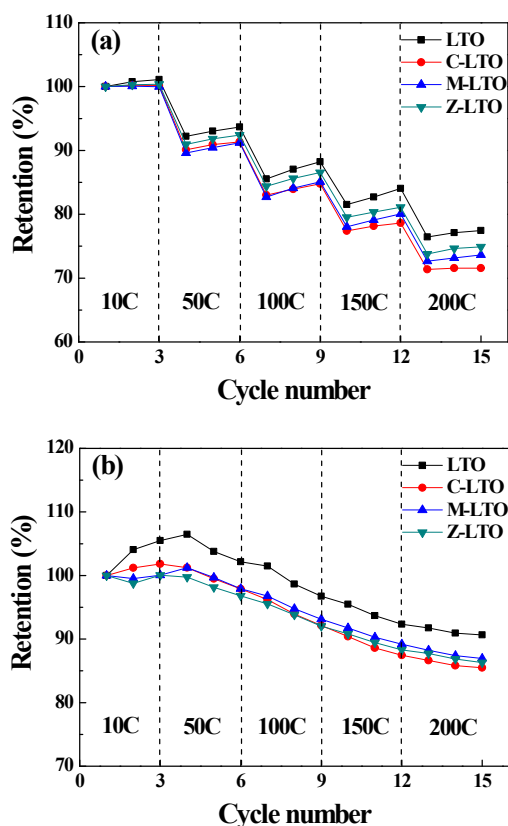


Fig. 4. The cycle performance of the hybrid capacitor employing different coating materials at different current rates ((a) discharge capacity, (b) DC-ESR)

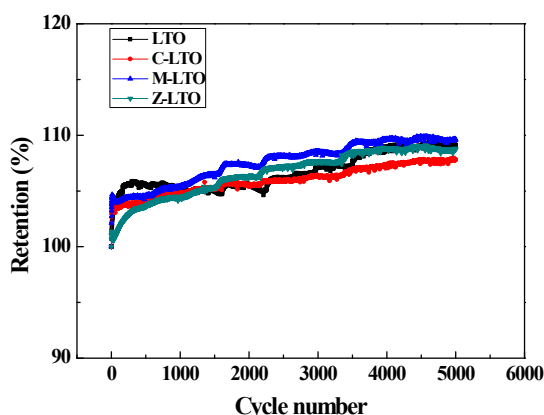


Fig. 5. The cycle performance of the hybrid capacitor prepared by employing different coating materials

With an increasing charge-discharge current, discharge capacity and DC-ESR retention of hybrid capacitor was decreased. With an increase in charge-discharge current, increase in difference in discharge capacity retention of LTO and surface coated LTO was observed due to the hindrance caused by lithium-ion intercalation and extraction by coating materials on LTO surface.

The discharge capacity retention of the hybrid capacitor at 50C at 25°C is shown in Fig. 5. The 5000th discharge capacity retentions were 109 %, 108 %, 110 % and 109 % for LTO, C-LTO, M-LTO, Z-LTO samples, respectively. The discharge capacity retention of hybrid capacitor of the

Table 1. The capacitance and equivalent series resistance of the hybrid capacitor prepared by employing different coating materials

Name of sample	Capacitance (F)	DC-ESR (mΩ)	AC-ESR (mΩ)
LTO	250.42	15.40	10.00
C-LTO	246.91	16.97	10.51
M-LTO	241.06	17.27	10.08
Z-LTO	237.49	15.82	10.26

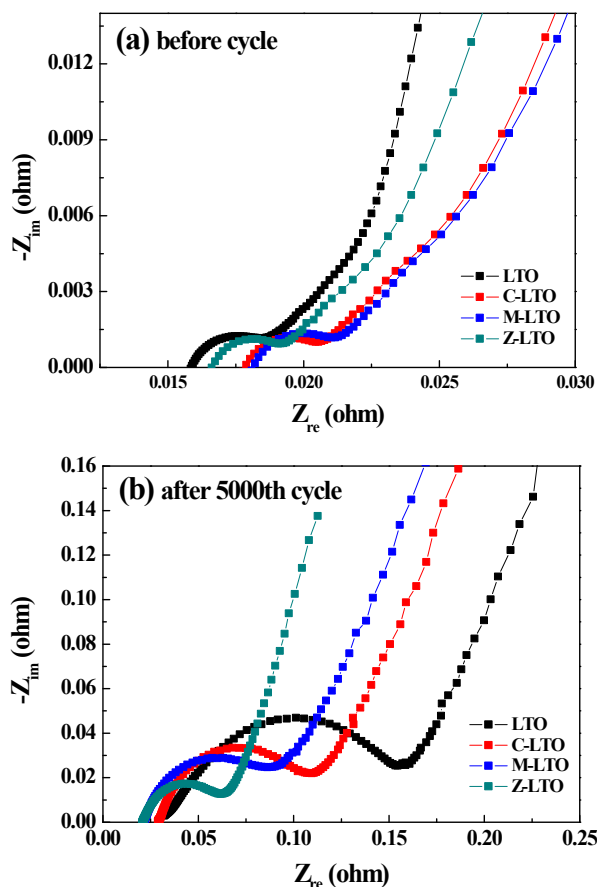


Fig. 6. AC Impedance spectra of the hybrid capacitor with different coating materials over a frequency range of 10⁻² to 10³Hz ((a) before electrochemical cycle, (b) after 5000th electrochemical cycle)

LTO and surface coated LTO exhibited remarkable change based on employment of different coating materials.

Fig. 6 shows the AC impedance spectra of hybrid capacitor both before and after the cycle test. Before electrochemical cycle test, LTO and surface coated LTO plots comprised of a high-frequency semi-circle followed by the low-frequency data in the form of a large and incomplete circle. According to Aurbach's discussion concerning the electrochemical impedance spectroscopy of LTO [10, 11], the high frequency semicircle in the spectra is attributed to Li-ion migration through surface, and the low-frequency one reflects charge transfer resistance. As per the comparison between the size of low frequency semi circles after charge and discharge cycle for 5000th, it is ascertained that the surface coated LTO exhibits a much smaller radius than that of LTO. This demonstrates that the surface coating can effectively prevent direct exposure of charged LTO to the liquid electrolyte during the high-voltage cycling, which in turn mitigates the decomposition of the liquid electrolyte on the delithiated LTO surface [12].

Fig. 7 illustrates the photographs of cylindrical cell before and after the electrochemical cycle test. With an increase in cycle number, the base of cylindrical cell exhibited swelling due to gas generation from reaction between LTO and electrolyte. Table 1 show the rough cycle

number, when cylindrical cell was swollen. The swelling cycle number of surface coated LTO was higher than that of LTO. The surface coating is employed as a barrier layer to control the gassing reaction by isolating the LTO particle from electrolyte solution [8].

4. Conclusion

In this study, the effects of surface coating on the electrochemistry properties and gas generation of LTO was investigated. The capacitance of LTO was observed to be higher than that of surface coated LTO and the ESR of LTO was lower than that of surface coated LTO. These results could be attributed to the obstruction of coating layer on lithium ion insertion and extraction process. The discharge capacity and DC-ESR retention as a function of different current rates showed a similar tendency. The swelling cycle number of surface coated LTO was higher than that of LTO. The surface coating is employed as a barrier layer to control the gassing reaction by isolating the LTO particle from electrolyte solution.

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Table 2. The swelling cycle number of the hybrid capacitor prepared by employing different coating materials

Name of Sample	Cycle number
LTO	4200
C-LTO	4900
M-LTO	5350
Z-LTO	5500

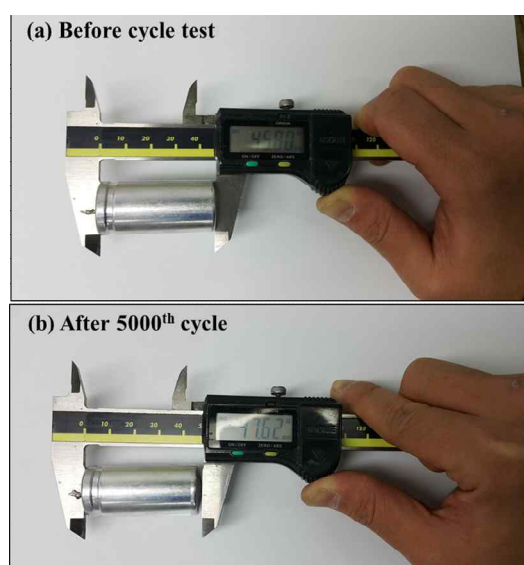


Fig. 7. The photographs of cylindrical cell of the electrochemical cycle test ((a) before electrochemical cycle, (b) after 5000th electrochemical cycle)

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