

Effect of Al modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode/activated carbon cathode for advanced hybrid supercapacitors

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In this paper, we successfully fabricated Al-modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in one-step, easily, simply, and quickly. The structural properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ by Al modification were favorable to electrochemical activity compared to pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$, and thus, it was confirmed that electrochemical performances such as cell balancing and initial discharge capacitance were effectively improved. The optimized anode/cathode thickness was selected 70 μm /240 μm . Al modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ realized high discharge capacitance of 61 F/g. Therefore, Al modification can be considered as one of the effective methods for the electrochemical performances of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes for next-generation hybrid supercapacitors.

Key words: $\text{Li}_4\text{Ti}_5\text{O}_{12}$, Al modification, Optimized anode/cathode thickness, Hybrid supercapacitors.

Introduction

Currently, with interest in electric vehicles, electric motorcycles, uninterruptible power supplies, and new and renewable energy, research on energy storage devices such as lithium-ion batteries, supercapacitors, and fuel cells is being actively conducted [1, 2]. Until now, lithium-ion batteries have been applied in most places due to their high energy density, but studies are being conducted to prevent safety accidents such as low power density, short lifespan, and fire and explosion. However, there is a limit to reliably solving these shortcomings in terms of the energy storage mechanism of the lithium-ion battery. Therefore, although the energy density is low, studies on high power density, infinite lifespan, and safe supercapacitors are in progress. Recently, in order to improve the low energy density of the existing supercapacitor, interest in a hybrid supercapacitor using a lithium ion battery and an electrode of a supercapacitor one by one is increasing [3-5]. The hybrid supercapacitors are designed to combine the advantages of supercapacitors and lithium-ion batteries.

Among the various components, it is the anode that affects the electrochemical performances of hybrid supercapacitors. Among various anode candidates such as TiO_2 , $\text{H}_2\text{Ti}_{12}\text{O}_{25}$, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, Nb_2O_5 , $\alpha\text{-Fe}_2\text{O}_3$, LiCrTiO_4 ,

MoO_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is the most promising anode candidate because it possesses almost infinite lifetime by zero-strain [1-3]. However, since $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is also an insulator with low conductivity, studies such as morphology control, doping, and coating are being conducted to improve it. Among them, doping is the easiest and most effective way to definitely improve electrochemical performances [3, 6]. Therefore, studies have been reported to improve the electrochemical performance by doping cations such as Cr, Ni, Sr, Ta and La and anions such as F and Br.

In this paper, an Al modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode was fabricated using Al_2O_3 , one of the most economical materials among various dopants, to fabricate a hybrid supercapacitor.

Experimental

Granuel- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder was prepared via spray drying method with precursor slurry and afterwards sintered in air at 790 °C for 8 h. The precursor slurry was fabricated using Li_2CO_3 and TiO_2 . The molar ratio of Li_2CO_3 and TiO_2 was 4:5. The powder was mixed in ethyl alcohol for 20 h with ZrO_2 ball for homogeneous mixing. The slurry was atomized at 205 °C via a two-fluid nozzle with atomizing pressure (3.8 kg/cm²). The commercial activated carbon was selected as a cathode of hybrid supercapacitors. For Al-modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$, the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Al_2O_3 are mixed in a weight ratio of 99.5 to 0.5, and heat treatment was performed at 790 °C for 3 h.

The Al-modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode was produced by the subsequent process: to prepare a slurry, anode powder, conductive Super P (carbon black) and

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polyvinylidene fluoride (PVDF) binder were blended with a weight ratio of 85:6:9. The N-Methyl pyrrolidone (NMP) was added for slurry formation. The weights of cathode and anode were 2.8 g and 3.2 g, respectively. The blended slurry was cast on Al foil with 110 μm thickness and then dried at 100 $^\circ\text{C}$ to eliminate the NMP. The Al foil was compressed with 75-85 μm thickness. After that, the hybrid supercapacitor was dried in a vacuum oven for 40 h to eliminate the moisture and impregnated with a 1.7 M LiBF_4 solution in dimethyl carbonate (DMC):ethylene carbonate (EC).

The crystallinity and microstructure of the pristine and Al modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles were measured via X-ray diffraction (XRD) and field emission scanning electron microscope (FESEM). The electrochemical performances were confirmed by an Arbin BT 2042 in the voltage range of 0-2.8 V.

Results and Discussion

Figure 1 shows the XRD patterns of Al-modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The (111), (311), (400), (331), (511), (440) and (531) peaks with cubic spinel structure (Fd3m space group) are located at 18.8, 35.2, 43.4, 47.7, 57.2, 62.9 and 66.3, respectively (JCPDS file no. 26-1198) [4]. This result is consistent with the typical $\text{Li}_4\text{Ti}_5\text{O}_{12}$ peaks. Also, no significant secondary peaks is confirmed. As a result, it can be inferred that Al-modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is successfully synthesized. As shown in Fig. 1(b), we can confirm that the (111) peak of Al-modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is shifted to a lower angle compared to pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which indicates successful modification of Al. The some of Al^{3+} (0.52 \AA) of Al-modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ leads to reduction/oxidation of $\text{Ti}^{4+}/\text{Ti}^{3+}$, indicating charge compensation. It can change the lattice plane of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ since the Ti^{4+} and Ti^{3+} have

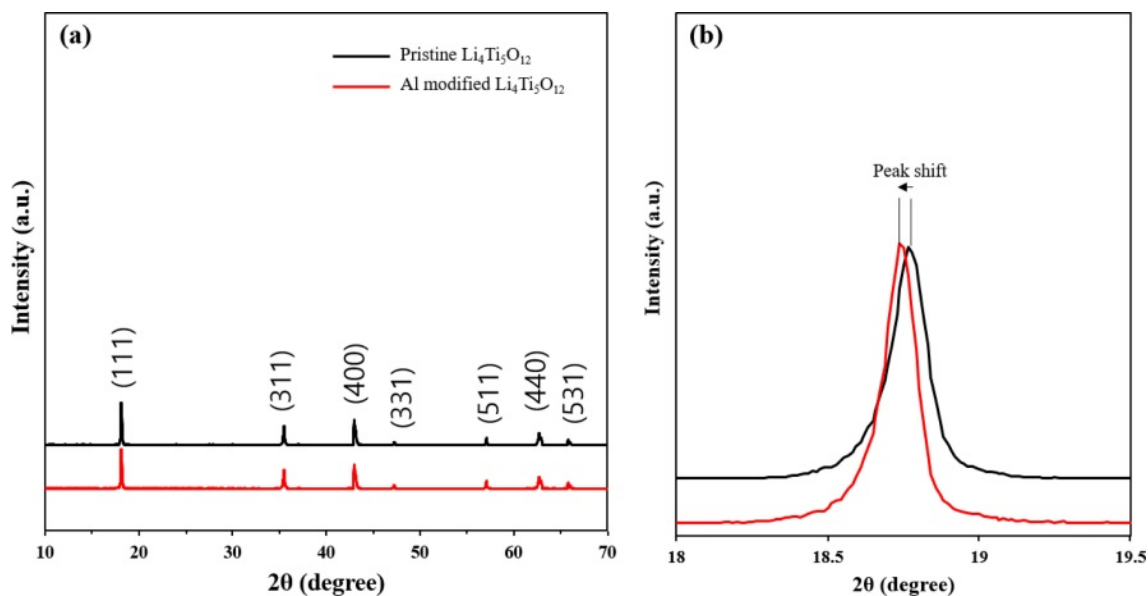


Fig. 1. XRD pattern of Al modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

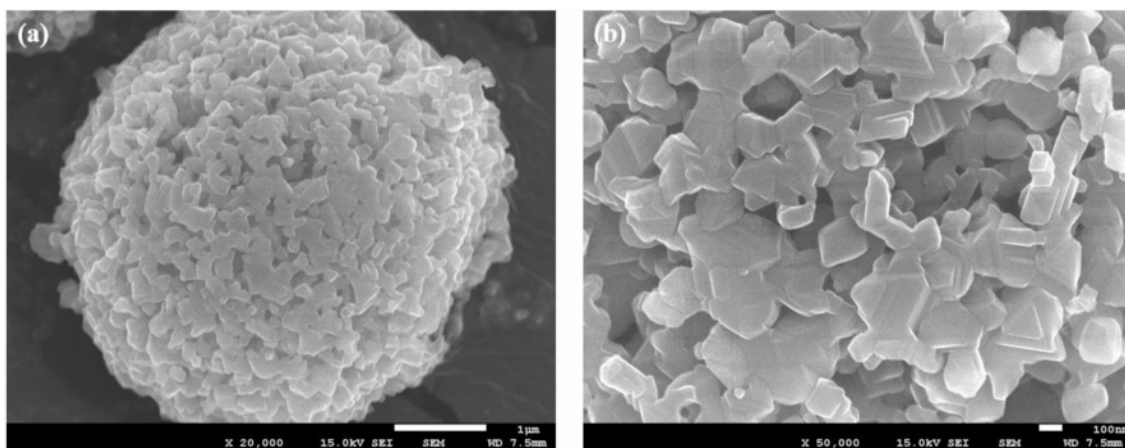


Fig. 2. FESEM images of Al modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

Table 1. Discharge capacitance retention of Al modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with different anode/cathode thickness.

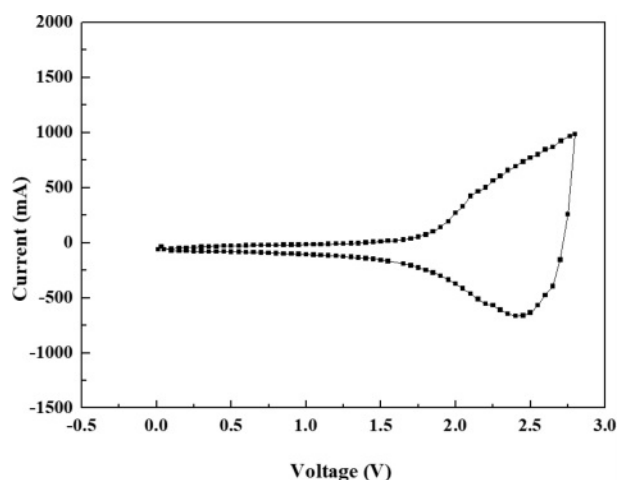
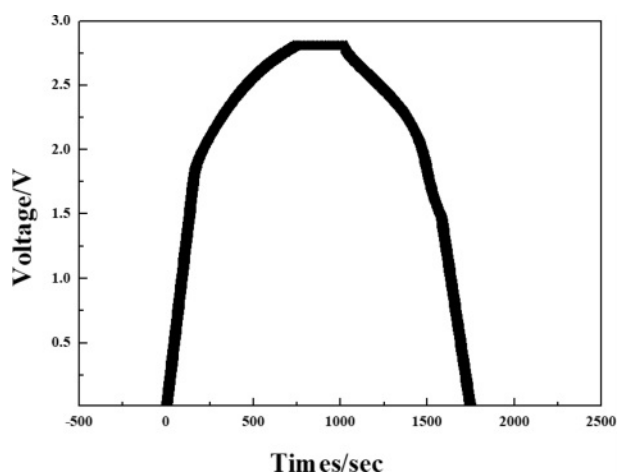
Anode / cathode thickness	0.1 A/g	0.5 A/g	1.0 A/g	2.0 A/g	3.0 A/g
90 μm / 240 μm	100 (64 F/g)	94 %	87 %	70 %	69 %
90 μm / 180 μm	100 (59 F/g)	96 %	88 %	71 %	70 %
70 μm / 240 μm	100 (61 F/g)	97 %	91 %	74 %	72 %
70 μm / 180 μm	100 (54 F/g)	95 %	88 %	71 %	69 %
50 μm / 240 μm	100 (56 F/g)	95 %	89 %	71 %	70 %
50 μm / 180 μm	100 (46 F/g)	91 %	84 %	68 %	66 %
40 μm / 240 μm	100 (51 F/g)	92 %	86 %	69 %	68 %
40 μm / 180 μm	100 (45 F/g)	92 %	85 %	68 %	67 %

different ionic radii of 0.68 Å and 0.76 Å, respectively. The bigger lattice parameters spacing via Al substitution, resulting in rapid lithium ion transfer.

Figure 2 shows the microstructure and morphology of Al-modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Al-modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has a spherical shape like typical $\text{Li}_4\text{Ti}_5\text{O}_{12}$, and the size of secondary particles is about 4.8 μm . The secondary particles consist of numerous primary particles with 300-500 nm. In general, such porous structure of Al-modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in with numerous pores is thought to facilitate fast and smooth movement of lithium ions and electrons due to sufficient wetting of the electrolyte [5, 6].

In order to measure the electrochemical performances of the hybrid supercapacitor with Al-modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode, the discharge capacitance retention with the various electrode thickness, as shown in Table 1. The capacity retention tends to decrease as the electrode thickness increases. When the current density of 0.1 A/g, the capacitance is proportional to the electrode thickness. It can be explained by sufficient movement of lithium ions and electrons. However, it can be confirmed that the capacitance decreases at high current density (1.0 A/g and 2.0 A/g). It is closely related to the relatively slower kinetics of lithium ions in the anode than BF_4^- ions in the cathode, which move relatively faster. Therefore, only the upper part of the anode participates in the electrochemical reaction. In the cathode, capacitance retention increases with thickness regardless of current density. As a result, the 90 μm anode and 240 μm cathode have the highest capacitance at 0.1 A/g, but have low capacitance retention at high current density. Therefore, 70 μm of anode and 240 μm of cathode were selected as thicknesses showing the optimal electrochemical performance (72 % at 3.0 A/g) [1, 2].

Figure 3 shows the cyclic voltammetry (CV) curves at a scan rate of 10 mV/s in the voltage of 0-2.8 V since working voltage of activated carbon (cathode) is 4.3 V and Al-modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (anode) is 1.5 V. The shape of CV curve is similar to the previously reported

**Fig. 3.** CV curves of Al modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$.**Fig. 4.** Initial charge-discharge profiles of Al modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

hybrid supercapacitors. The movement of lithium ions at the anode and BF_4^- ions at the cathode can be confirmed from the CV curve. Below a voltage of 1.5 V, a small and similar amount of charging and discharging occurs only by lithium ions. The BF_4^- ions at the cathode do not affect the capacitance. Therefore,

it is called the “mirror effect” [7, 8]. Above 1.5 V, both lithium ions and BF_4^- ions participate in electrochemical activity. Among them, BF_4^- ion is a major factor and lithium ion is a minor factor for capacitance. The oxidation and reduction peaks of the hybrid supercapacitors are about 2.52 V and 2.35 V, respectively. Such small polarization of the oxidation and reduction peaks indicates the excellent reversibility of the hybrid supercapacitors [9, 10]. In the CV curve, the inner area is proportional to the total capacitance of hybrid supercapacitor. Therefore, it can be inferred that Al modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can possess higher capacitance than pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$. This is because Al modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has greater electrical conductivity compared to pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

Figure 4 shows the initial charge-discharge curves of the hybrid supercapacitor with Al modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode/activated carbon cathode. The specific capacitance of the hybrid supercapacitor can be calculated using following equation [11, 12]:

$$C = \frac{q}{\Delta V \times m} = \frac{\int i \Delta t}{\Delta V \times m} \quad (1)$$

where ‘ C ’ is the capacitance, ‘ q ’ is the charge, ‘ ΔV ’ is the potential range, ‘ m ’ is the mass of the active materials, ‘ i ’ is the current, and ‘ t ’ is discharge time. The discharge capacitance of the hybrid supercapacitor with Al modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode/activated carbon cathode is 61 F/g at current density of 0.1 A/g. This capacitance is higher than that of conventional hybrid supercapacitors. This is related to the internal resistance called IR drops, which can be calculated as [13, 14]:

$$R = \frac{V_{\text{charge}} - V_{\text{discharge}}}{2I} \quad (2)$$

where ‘ V_{charge} ’ is the end charge voltage, ‘ $V_{\text{discharge}}$ ’ is the starting discharge voltage and ‘ I ’ is the current. The IR drop value of hybrid supercapacitor is 0.19 Ω at 0.1 A/g. It is well known that IR drop can affect the electrochemical performances. This is because IR drop is related to the different mechanism of both Faradaic process on anode and non-Faradaic process on cathode [15]. It is judged that the electrochemical properties have a positive effect by the low IR drop of Al modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

Conclusions

In this study, we successfully synthesized Al-modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$. In addition, an asymmetric hybrid supercapacitor was fabricated using an Al-modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode and an activated carbon cathode, and electrochemical performances such as cell balancing and initial discharge capacity were measured. Al-modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ displayed the identical crystal structure and morphology as $\text{Li}_4\text{Ti}_5\text{O}_{12}$. To optimize of electrochemical performances, capacitance retention was calculated with various thickness of anode and cathode. In addition, high initial discharge capacity and low IR drop were obtained through Al modification. As a result, we can conclude the Al modification as one of the methods that can compensate for the shortcomings of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode.

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