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# Improving rate capabilities of hybrid supercapacitor using Li<sub>4</sub>Ti<sub>5-x</sub>Zr<sub>x</sub>O<sub>12</sub>/activated carbon

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The  $Li_4Ti_{5-x}Zr_xO_{12}$  (x = 0, 0.15, 0.3, 0.45 and 0.6) anodes were prepared using a simple solid-state method. We investigated the electrochemical performance of hybrid supercapacitor using  $Zr^{4+}$  doped  $Li_4Ti_5O_{12}$  anode and activated carbon cathode. When Zr entered  $Li_4Ti_5O_{12}$ , the higher lattice parameters and conductivities of  $Li_4Ti_{5-x}Zr_xO_{12}$  (x = 0.15, 0.3, and 0.45) obviously improved the electrochemical performance of hybrid supercapacitor. Among them, the  $Li_4Ti_{5-x}Zr_xO_{12}$  anode has a superior specific capacitance of 69 Fg<sup>-1</sup> at 0.5 Ag<sup>-1</sup> rates. Also, the power and energy densities were 212.3 W kg<sup>-1</sup> and 65.2 Wh kg<sup>-1</sup>, respectively.

Key words: Hybrid supercapacitor, Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, Zr Doping, Power and energy densities.

### Introduction

Recently, all over the world, the demand of the environment friendly policy and the renewable energy are growing. Therefore, the development necessity of the next generation energy storage device has increased. The supercapacitor is the one of a variety of the energy storage devices. The supercapacitor is charged and discharged when ions are an adsorptiondesorption on the surface of electrode material. The supercapacitor has high power density  $(10^3-10^4 \text{ Wkg}^{-1})$ , the fast charge-discharge rate and the long cycle life [1-3]. However, the supercapacitor has relatively low energy density [4, 5]. The energy device of other types, lithium ion batteries (LIBs) stored an energy when lithium ions are inserted-extracted. Lithium ion batteries with a high energy density (150-200 Wh kg<sup>-1</sup>) [6], have used with power sources such as mobile phone, PC and digital camera over the last decade. Lately, it has been expanded for applications in hybrid electrical vehicles and an electrical vehicles. However, the safety, cycle performance and power density of the present are not perfect yet [7, 8]. In order to overcome some of the problems, recently, a new energy device called the hybrid supercapacitor has been attracting attention. Hybrid supercapacitors are energy storage devices which combine the advantages of the lithium ion batteries and the supercapacitors [6, 9]. It is composed of the electrode materials of the anode and cathode used in the lithium ion batteries and the

supercapacitors, respectively. Hybrid supercapacitor shows the high power density at cathode during an adsorption-desorption process by the electric double layer reaction. Another electrode implemented the higher capacity when lithium ions are insertedextracted into the interior of the anode. Therefore, hybrid supercapacitors have advantages such as the high energy density, the superior power density, long cycle life [10]. Hybrid supercapacitor is fabricated in a variety of ways anode hybrid or cathode hybrid and materials [11-16]. Among the various materials, spinel L4iTi5O12 (hereafter LTO) is attracted attention and mainly applied in the anode material. The L<sub>4</sub>iTi<sub>5</sub>O<sub>12</sub> is well known to have zero-strain in unit cell volume during the intercalation/deintercalation of Li<sup>+</sup> ion [15]. Also, electrochemical theoretical capacity of L<sub>4</sub>iTi<sub>5</sub>O<sub>12</sub> is 175 mAh/g<sup>-1</sup>, and Spinel  $L_4iTi_5O_{12}$  can prevent the form a solid electrolyte interface (SEI) [17] because it has a flat Li insertion potential at about 1.55 V (versus  $Li^+/Li$ ) [13, 17, 18]. However, the slow  $Li^+$  ion diffusion coefficient ( $< 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ ) [19] and poor electron conductivity  $(2.65 \times 10^{-7} \text{ S cm}^{-1})$  [14] of L4iTi5O12 are limited to a variety applications. To improve the disadvantages of the Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, various methods have been investigated such as doping with metal ions (Zr<sup>4+</sup> [19-21], Zn<sup>2+</sup> [22], Al<sup>3+</sup> [21], La<sup>3+</sup> [23], Ta<sup>5+</sup> [24], Cr<sup>3+</sup> [25], Ni<sup>3+</sup> [25], Na<sup>+</sup> [26], V<sup>5+</sup> [27],  $Mg^{2+}$  [28],  $Nb^{5+}$  [29],  $Mo^{4+}$  [30], and  $Mo^{6+}$  [30]) or non-metal ions (F<sup>-</sup> [31] and Br<sup>-</sup> [32]), synthesizing nano-sized particles, coating carbon on the surface of the particles, and mixing carbon with the particles [16]. Among these methods,  $Li_4Ti_5O_{12}$  with dopants such as  $Zr^{4+}$ ,  $Zn^{2+}$ ,  $Mg^{2+}$ ,  $Al^{3+}$ ,  $Ni^{3+}$  on the  $Ti^{4+}$  sites can increase in the amount of Ti3+/Ti4+ mixing through

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**Fig. 1.** (a) XRD patterns of the  $Li_4Ti_{5-x}Zr_xO_{12}$  ( $0 \le x \le 0.6$ ) powders. (b) Enlarged XRD patterns between 17 and 20 degrees.

**Table 1.** Lattice parameter of the  $Li_4Ti_{5-x}Zr_xO_{12}$  ( $0 \le x \le 0.6$ ) anode materials.

Compounds	Lattice parameter (Å)
Li <sub>4</sub> Ti <sub>4.4</sub> Zr <sub>0.6</sub> O <sub>12</sub>	8.37327
Li <sub>4</sub> Ti <sub>4.55</sub> Zr <sub>0.45</sub> O <sub>12</sub>	8.38688
Li <sub>4</sub> Ti <sub>4.7</sub> Zr <sub>0.3</sub> O <sub>12</sub>	8.34189
Li <sub>4</sub> Ti <sub>4.85</sub> Zr <sub>0.15</sub> O <sub>12</sub>	8.31035
$Li_4Ti_5O_{12}$	8.29699

charge compensation. Therefore, electronic conductivity is increased [20]. In addition, Yi *et al.* [19] reported that  $Zr^{4+}$ doping can be improved the rate ability and cycling stability of L<sub>4</sub>iTi<sub>5</sub>O<sub>12</sub> due to the reduction of charge transfer resistance and increased lithium diffusivity. Also, the surface area is increased with reducing the particles size by doping system [20], which lead to fast Li<sup>+</sup> ion diffusion due to shorter diffusion [19, 20, 33-36]. In this paper, we assembled the cylindrical type hybrid supercapacitor using  $Zr^{4+}$ doped Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> and activated carbon as anode and cathode, respectively, and investigated the effect for different  $Zr^{4+}$ -doping content on the structural properties and electrochemical performance of hybrid supercapacitor.

## **Experiments**

Spinel-Li<sub>4</sub>Ti<sub>5-x</sub>Zr<sub>x</sub>O<sub>12</sub> ( $0 \le x \le 0.6$ ) samples were fabricated using solid-state methods with Li<sub>2</sub>CO<sub>3</sub> (Junsei, 99%), TiO<sub>2</sub> (Junsei, 99%), and ZrO<sub>2</sub> (Fluka, 99%) as raw materials. The powders were mixed in ethyl alcohol for 24h in a ball mill and calcined at 800°C for 6h in air. We used X-ray diffraction (XRD) to analyze the crystallinity. The anode of the hybrid capacitor was composed of Li<sub>4</sub>Ti<sub>5-x</sub>Zr<sub>x</sub>O<sub>12</sub>, conductive carbon black binder (Super P), and polyvinylidene fluoride (PVDF) in the weight ratio 83 : 7 : 10. N-Methyl pyrrolidinine (NMP) as a solvent was coated on aluminum foil to a thickness of 125 µm using a bar coater and then dried at 100 °C to remove the NMP solvent. The material was then pressed to a thickness of 70-80 µm. The width of the cathode, separator, and anode were 28 cm, 40 cm, and 30 cm, respectively and the height of the cathode and anode were both 3 cm. The prepared electrodes and separator were assembled into a cylindrical cell (outer diameter of 2 cm × height of 4.5 cm) in an argon-gas-filled glove box. Before being impregnated with a 1.5M solution of LiBF<sub>4</sub> as the electrolyte, the cell was dried in a vacuum oven for 48 h to get rid of the moisture. The galvanostatic chargedischarge tests (initial capacitance, rate capability) were carried out using Arbin BT 2042 battery test system at various current densities with a cut off voltage of 0-2.8 V. The electrochemical impedance spectroscopy (EIS) was done in the frequency range of  $10^{-1}$  to  $10^{-6}$  Hz.

# **Results and Discussion**

Fig. 1 (a) show the x-ray diffraction patterns of the  $Li_4Ti_{5-x}Zr_xO_{12}$  ( $0 \le x \le 0.6$ ). All main peaks of  $Li_4Ti_{5-x}Zr_xO_{12}$ <sub>x</sub>Zr<sub>x</sub>O<sub>12</sub> are similar to the cubic spinel structure with Fd3m space group of pristine Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (PDF No, 49-0207). The x-ray diffraction patterns of the  $Li_4Ti_{5-}$  $_{x}Zr_{x}O_{12}$  ( $0 \le x \le 0.45$ ) were not observed the secondary phases because the Zr<sup>4+</sup> is successfully substituted into the lattice of the pristine Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>. On the contrary, Li<sub>4</sub>Ti<sub>4.4</sub>Zr<sub>0.6</sub>O<sub>12</sub> was observed the secondary phases by excessive  $Zr^{4+}$  contents of 0.6 mol %. Fig. 1 (b) shows the (111) planes of the  $Li_4Ti_{5-x}Zr_xO_{12}$  below X = 0.6. The peaks of the samples shifted toward lower degrees with increasing of  $Zr^{4+}$  dopant. This indicates that the lattice parameter of the  $Li_4Ti_5O_{12}$  is increased when the  $Ti^{4+}$  (0.605 Å) is substituted by  $Zr^{4+}$ (0.80Å) with the larger radius than that of Ti4+, as calculated using Bragg's equation (1). Bragg's equation is used to calculate the plane spacing 'd' of  $Li_4Ti_{5-x}Zr_xO_{12}$  ( $0 \le x$  $\leq 0.6$ ) as follows [37]:

$$2d\,\sin\theta = n\lambda\tag{1}$$

The lattice parameter '*a*' for the cubic structure of  $Li_4Ti_{5-x}Zr_xO_{12}$  ( $0 \le x \le 0.6$ ) was calculated using the following equation:

$$a = \sqrt{h^2 + k^2 + 1^2} \tag{2}$$

Here, 'd' is the spacing between the planes in the atomic lattice. 'h', 'k', and 'l' are miller indices of the crystal planes [38]. The lattice parameter of high angle reflection is dependable, while value slightly varies depending on different orientation of samples, caused by diffusion and absorption of the X-ray beams' refraction from the samples [38]. The corrected lattice parameter can be obtained to reduce errors of measured ' $\theta$ ' and 'd' value by using the Nelson-Riley formula:

$$f(\theta) = \frac{1}{2} \left( \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$$
(3)

The corrected lattice parameter of  $Li_4Ti_{5-x}Zr_xO_{12}$  ( $0 \le x \le 0.6$ ) is depicted in Table 1. This shows that the expanded channel by  $Zr^{4+}$ -doping improve the  $Li^+$  ion diffusion and the electrochemical properties [39, 40].

Fig. 2 show the initial charge-discharge curves of the hybrid supercapacitors using Li4Ti5-xZrxO12 below x = 0.6 anode at 0.5 Ag<sup>-1</sup> from 1.5 to 2.8 V. Typically, the initial charge-discharge curve of supercapacitor shows the symmetrical triangle shape. However, the hybrid supercapacitor consists of anode and cathode which are different in reaction mechanism. Thus, the hybrid supercapacitor shows the initial chargedischarge curves of an asymmetric shape. The initial discharge capacitance was increased with increasing the  $Zr^{4+}$  contents below x = 0.45. However, discharge capacitance of  $Zr^{4+}$  contents above x = 0.6 is lower than the discharge capacitance of  $Zr^{4+}$  contents with x = 0.3, 0.45, respectively. The IR drop is confirmed at the discharge slop from 2.8 to 1.5 V as seen in Fig. 6(b). This is occurred owing to the internal resistance, especially, shows kinetics of  $Li^+$  ion at anode [41]. The IR drop of hybrid supercapacitor can be calculated



**Fig. 2.** Electrochemical impedance spectra (EIS) curves for the  $Li_4Ti_{5-x}Zr_xO_{12}$  ( $0 \le x \le 0.6$ ) anode materials.

using the following equation [42]:

$$R = \frac{V_{charge} - V_{discharge}}{21}$$
(4)

Where, 'V<sub>charge</sub>' is the cell voltage at the end of charge, 'V<sub>discharge</sub>' is the cell voltage at the beginning of the discharge, and 'I' is the absolute value of the current, which is the same during the charge and the discharge. The IR drops of the  $Li_4Ti_{5-x}Zr_xO_{12}$  below x = 0.6 were calculated by the equation, to be 0.0115, 0.00815, 0.0071, 0.0056 and 0.01112  $\Omega$ , respectively. It can be confirmed that the IR drop was decreased with increasing the Zr<sup>4+</sup> content. Therefore, a decreased IR drop of the  $Li_4Ti_{5-x}Zr_xO_{12}$  below x = 0.45 means that the performance of charge-discharge is improved due to enhanced conductivity. However, the IR drop of Li<sub>4</sub>Ti<sub>4.4</sub>Zr<sub>0.6</sub>O<sub>12</sub> shows the larger than that of Li<sub>4</sub>Ti<sub>5-x</sub>  $Zr_xO_{12}$  with x = 0.3 and 0.45. Because the Li<sub>4</sub>Ti<sub>4.4</sub>Zr<sub>0.6</sub>O<sub>12</sub> has lower conductivity than that of  $Li_4Ti_{5-x}Zr_xO_{12}$  with x = 0.3 and 0.45, respectively. The specific capacitances of  $Li_4Ti_{5-x}Zr_xO_{12}$  below x = 0.6 shows a 38, 51, 62, 69 and 58  $Fg^{-1}$ , respectively at 0.5  $Ag^{-1}$  rates.

Fig. 3 shows the electrochemical impedance spectroscopy (EIS) curves of  $Li_4Ti_{5-x}Zr_xO_{12}$  (0.15  $\leq x \leq 0.45$ ) after charging at 2.8 V. The EIS curve can be categorized into two parts: a semicircle, and a straight line forming an angle of 45 degrees. The semicircle is situated in high to medium frequency region that corresponds to Li<sup>+</sup> ions diffusion at the electrode/electrolyte interface [43]. In the high to medium frequency region,  $R_s$ presents the ohmic resistance of the electrolyte and R<sub>et</sub> shows charge-transfer resistance at the active material interface [43]. The straight line located in the low frequency region is called Warburg impedance cause by the semi-infinite diffusion of Li<sup>+</sup> ion in the electrode [17]. The measured  $R_{ct}$  of  $Li_4Ti_{5-x}Zr_xO_{12}$  is 99, 74, 53, 47 and 91 mΩ, respectively. The  $R_{ct}$  of the  $Li_4Ti_{5\text{-}x}$  $Zr_xO_{12}$  (0.15  $\leq x \leq 0.6$ ) is lower than  $R_{ct}$  of the pristine  $Li_4Ti_5O_{12}$ . The  $Zr^{4+}$  doping influenced the enhancement of electron conductivity and ionic conductivity. We can assume that ionic conductivity was improved by the expanded lattice. Therefore, hybrid supercapacitor using the Li<sub>4</sub>Ti<sub>4.55</sub>Zr<sub>0.45</sub>O<sub>12</sub> anode was obtained by the better cycle performance with the lower R<sub>ct</sub>. However, the excessive Zr4+ content increased the Rct of Li4Ti5-x  $Zr_xO_{12}$ . From Table 2, the Li<sup>+</sup> ions diffusion coefficient  $(D_{\rm Li})$  of the Li<sub>4</sub>Ti<sub>5-x</sub>Zr<sub>x</sub>O<sub>12</sub> anode can be observed the following equation [20]:

$$D_{Li} = 0.5 \left(\frac{RT}{AF^2 \sigma_W C}\right)^2$$
(5)

Here, '*R*' is the gas constant, '*T*' is the absolute temperature, ' $\sigma_w$ ' is Warburg impedance coefficient, '*F*' is Faraday's constant, '*A*' is the contact area of the electrode surface and '*C*' is the molar concentration of Li<sup>+</sup> ions. The  $D_{\text{Li}}$  of the Li<sub>4</sub>Ti<sub>5-x</sub>Zr<sub>x</sub>O<sub>12</sub> below x = 0.6 are  $1.632 \times 10^{-9}$ ,  $1.184 \times 10^{-8}$ ,  $5.345 \times 10^{-8}$ ,  $6.715 \times 10^{-8}$ 

and  $7.125 \times 10^{-9}$  cm<sup>2</sup>/s, respectively. It is obvious that increasing  $D_{\text{Li}}$  can be attributed to the Zr<sup>4+</sup> ions dopant. We can infer that Zr<sup>4+</sup>-doping enhanced the conductivity expected to affect rate capability of hybrid supercapacitor. Also, this phenomenon is consistent with results in Figure 2.

Fig. 4 shows the rate capabilities of the Li<sub>4</sub>Ti<sub>5-x</sub>Zr<sub>x</sub>O<sub>12</sub> ( $0 \le x \le 0.6$ ) at different rates from 1.0 to 3.0 Ag<sup>-1</sup>. There is no difference in the initial retention of samples at 1.0 Ag<sup>-1</sup>. However, the retention of Li<sub>4</sub>Ti<sub>5-x</sub>Zr<sub>x</sub>O<sub>12</sub> below x = 0.6 was less decreased than x = 0.6 with increasing the current density. All samples have retentions of more than 48% at 3.0 Ag<sup>-1</sup>. Among them, the Li<sub>4</sub>Ti<sub>4.55</sub>Zr<sub>0.45</sub>O<sub>12</sub> shows the best retention of more than 60%. The Zr<sup>4+</sup> doping significantly enhanced the rate capability than pristine Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> at high current density.

The ragone plots of the hybrid supercapacitor using the  $Li_4Ti_{5-x}Zr_xO_{12}$  anode is shown in Fig. 5. The power density and energy density were calculated by following equations [44].



**Fig. 3.** Different charge-discharge rates of the hybrid supercapacitors using the  $Li_4Ti_{5-x}Zr_xO_{12}$  ( $0 \le x \le 0.6$ ) anode materials from 1 to 3 Ag<sup>-1</sup>.



**Fig. 4.** (a) Initial charge-discharge curves of the hybrid supercapacitors using  $\text{Li}_4\text{Ti}_{5-x}\text{Zr}_x\text{O}_{12}$  ( $0 \le x \le 0.6$ ) anode materials. (b) Initial charge-discharge curves between 2.6 and 2.9 V.



Fig. 5. Ragone Plots of the hybrid supercapacitors using  $Li_4Ti_{5-x}$   $Zr_xO_{12}$  ( $0 \le x \le 0.6$ ) anode materials.

$$\mathbf{P} = \Delta \mathbf{V} \times \frac{\mathbf{i}}{\mathbf{m}} \tag{6}$$

$$E = P \times \frac{t}{3600}$$
(7)

$$\Delta V = \frac{(E_{\text{max}} + E_{\text{min}})}{2}$$
(8)

Were 'P' is the power density, 'E' is the energy density, ' $E_{max}$ ' is the voltage at the beginning of the discharge, ' $E_{min}$ ' is the voltage at the end of the discharge, 'I' is the discharge current, 't' is the discharge time, and 'm' is the total mass of electro active materials in both anode and the cathode. The hybrid supercapacitor using Li<sub>4</sub>Ti<sub>5-x</sub>Zr<sub>x</sub>O<sub>12</sub> anode exhibited an energy density ranging from 9.8 to 65.2 Whkg<sup>-1</sup> and power density ranging from 212.3 to 5982.4 W kg<sup>-1</sup>. In order to prove the superior performance of the Li<sub>4</sub>Ti<sub>5-x</sub>Zr<sub>x</sub>O<sub>12</sub>/activated carbon, our composition was compared with other asymmetric systems. It can be seen that the Li<sub>4</sub>Ti<sub>5-x</sub>Zr<sub>x</sub>O<sub>12</sub>/ activated carbon show better energy and power density than the asymmetric systems such as LTO/AC [45], C-LTO/AC [46], C-LTP/AC [47] and TNW/CNT [48].

#### Conclusions

In this study, we investigated the structural characteristics and electrochemical performance of hybrid supercapacitor using  $Li_4Ti_{5-x}Zr_xO_1$ /activated carbon. When  $Zr^{4+}$  entered  $Li_4Ti_5O_{12}$ , the  $Zr^{4+}$  doping increased the lattice parameter of  $Li_4Ti_5O_{12}$ . We can confirm that diffusion coefficient of  $Li^+$  was increased by lattice parameters. The hybrid supercapacitor using  $Li_4Ti_{5-x}Zr_xO_{12}$  (x = 0.15, 0.3, and 0.45) obviously improved the rate capability related charge transfer resistance. The power and energy density of hybrid supercapacitor using  $Li_4Ti_{4.55}Zr_{0.45}O_{12}$  were 212.3 W kg<sup>-1</sup> and 65.2 Wh kg<sup>-1</sup>, respectively. However, excessive  $Zr^{4+}$  doping of x = 0.6 cause a negative effect on the structure and electrochemical performance. We concluded that the hybrid supercapacitor using  $Li_4Ti_{4.55}Zr_{0.45}O_{12}$  can be

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regarded as a next generation energy storage device.

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