JOURNALOF

Ceramic Processing Research

# Preparation and application of urchin-like TiO<sub>2</sub>/activated carbon for high performance hybrid supercapacitors

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We successfully prepared urchin-like TiO<sub>2</sub> material composed of numerous nanorods by hydrothermal method. After that, a cylindrical hybrid supercapacitor was fabricated by using urchin-like TiO<sub>2</sub> anode and activated carbon cathode. The energy and power density of hybrid supercapacitor using urchin-like TiO<sub>2</sub> ranged from 10.134 to 50.648 Wh kg<sup>-1</sup> and from 194.412 to 12224.356 W kg<sup>-1</sup>, higher than those of hybrid supercapacitors using Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> anode. It also shows the extraordinary cycle performance of 93.6% at 3.0 Ag<sup>-1</sup> after 1000 cycles. As a result, we can conclude that urchin-like TiO<sub>2</sub> can be regarded as high efficiency anode for hybrid supercapacitors.

Key words: Urchin-like TiO<sub>2</sub>, Hydrothermal method, Hybrid Supercapacitor, Energy and power density.

#### Introduction

In recent years, the lithium ion batteries (LIBs) and supercapacitors have been widely used as an energy storage device. However, LIBs show low power density and cycle performance, though it has excellent energy density. In contrast, although the supercapacitors have attractive advantages of power density and cycle performance, it also has a critical drawback of low energy density. Therefore, in order to overcome the shortcomings of LIBs and supercapacitors, the hybrid supercapacitors, having asymmetry electrodes from both LIBs and supercapacitors, were designed to obtain positive synergetic effects [1, 2]. Moreover, according to the electronic power research institute (EPRI), the price of secondary batteries such as LIBs and lead storage battery is expensive and that of supercapacitors is relatively inexpensive [3]. In the long term, it offers a tremendous advantage for lowering the maintenance cost by reducing battery maintenance, control and replacement costs [4]. The usage of hybrid supercapacitors is even capable of reducing cost by half or more due to approximately 2.5 times higher energy density than supercapacitors [5]. Therefore, the hybrid supercapacitors can be regarded as a next generation energy storage device.

Among many materials, the  $Li_4Ti_5O_{12}$  (LTO) has a lower oxidation/reduction potential and "Zero-Strain" property, resulting in hardly expand its volume during charge-discharge process. Therefore, it has been highlighted as a long life anode material for energy storage devices. However, there are two main problems with LTO for use as an anode. First, LTO shows relatively low conductivity. As a result, initial capacitance loss occurs during charge-discharge process. Second, the LTO shows inferior theoretical capacity of 175 mAh g<sup>-1</sup> [6]. Therefore, alternative materials have been studied to replace the LTO. Recently, the urchin-like TiO<sub>2</sub> have attracted as an anode material due to of its high theoretical capacities of 335 mAh g<sup>-1</sup> [6, 7]. The electrochemical reaction of urchin-like TiO<sub>2</sub> can be expressed as the following equations [8]:

$$xLi^{+} + TiO_2 + xe^{-} \leftrightarrow Li_xTi_5O_2 (0 \le x \le 1)$$
(1)

Therefore, we assembled cylindrical hybrid supercapacitor composed of activated carbon (AC) as a cathode and urchin-like  $TiO_2$  as an anode and measured electrochemical performances to compare those of hybrid supercapacitor composed of AC and LTO.

## **Experimental**

Urchin-like TiO<sub>2</sub> materials were first prepared by the hydrothermal method. Simply, 15 mL deionized (DI) water, 15 mL hydrogen chloride (HCl) (36-38%), 0.6 g sodium chloride (NaCl), and 0.5 mL titanium (IV) n-butoxide 99% were mixed and stirred. After that, the mixture was transferred to a 100 mL Teflon-lined stainless steel autoclave, and kept at 150 °C for different reaction times. After cooling to room temperature, the resultant mixture was washed with DI water and dried at 100 °C. The prepared urchin-like TiO<sub>2</sub> and activated carbon were used as the anode and cathode, respectively. To prepare the urchin-like TiO<sub>2</sub> as the anode, the prepared

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powder, conductive carbon black (Super P), and polyvinylidene fluoride (PVDF) were mixed at the weight ratio of 83:7:10, and N-Methyl pyrrolidinine (NMP) solvent was added. The resultant slurry was cast on aluminum foil to a thickness of 125 µm using a bar coater, and then dried at 100 °C in order to remove the NMP. The aluminum foil was pressed to a thickness of about 70 µm. Subsequently, to eliminate moisture, the cell was dried in a vacuum oven for 48 hrs and impregnated with a 1.5 M LiPF<sub>6</sub> solution in 1:1 ethylene carbonate (EC): dimethyl carbonate (DMC) as the electrolyte. Lastly, the cathode, separator, and anode were assembled as a cylindrical cell in an argon-gas-filled glove box. The structural properties of the urchin-like TiO<sub>2</sub> particles were measured with X-ray diffraction (XRD) and a scanning electron microscope (SEM). The electrochemical performances were measured using an Arbin BT 2042 battery test system at various current densities ranging from 0.1 to 5 A  $g^{-1}$  with a voltage of 0-2.8 V. Electrochemical impedance spectroscopy (EIS) was conducted in the frequency range of  $10^{-1}$  to  $10^{-6}$  Hz.

## **Result and Discussion**

Figure 1(a) shows the XRD pattern of the synthesized urchin-like TiO<sub>2</sub> powder. The well-crystallized urchinlike TiO<sub>2</sub> powders were prepared via hydrothermal method. There were diffraction peaks were located at 27, 36, 41, 44, 54, 56, 63, 64 and 70°, which can be attributed to the (110), (101), (111), (210), (211), (220), (002), (310), (301) and (112) diffraction plane, indicating typical rutile TiO<sub>2</sub>. The microstructure of the urchinlike  $TiO_2$  powders were shown in Fig. 1(b). The average size of urchin-like TiO<sub>2</sub> powder is approximately 15.5 µm with a dense structure which is built by numerous nanorods with width diameter of 0.3 µm. The urchinlike structure can be obtained by chemical reactions and it is expected to bring positive effects to electrochemical performance of hybrid supercapacitors [10, 11]. The urchin-like  $TiO_2$  shows the high BET surface area of 120.387 m<sup>2</sup> g<sup>-1</sup> with pore volume of 0.5762 cm<sup>3</sup>  $g^{-1}$ . Therefore, we can infer that enlarged interface between electrode and electrolyte derived from high surface area electrode has a positive effect on electrochemical performance. The BET surface area was obtained by following equation [12, 13]:



**Fig. 1.** (a) XRD pattern and (b) microstructure of urchin-like TiO<sub>2</sub> powder.

$$\frac{p}{X_a(p_0-p)} = \frac{1}{X_m c} + \frac{c-1}{X_m c} \times \frac{p}{p_0}$$
(2)

where 'P' is the actual vapor pressure, ' $P_0$ ' is the vapor pressure at saturation, ' $X_m$ ' is the capacity of a single adsorption layer, ' $X_a$ ' is the adsorbed molecules on the sample, and 'C' is a constant.

Figure 2(a) shows the initial charge-discharge profiles of hybrid supercapacitors using LTO and urchin-like TiO<sub>2</sub> anode. Both curves show the trapeziform shape and current-resistance (IR) drop, different from typical supercapacitor curve. These are related with different mechanism between anode and cathode. The specific discharge capacitances of hybrid supercapacitors using LTO and urchin-like TiO<sub>2</sub> anode are 42 F g<sup>-1</sup> and 66 F g<sup>-1</sup> at 0.5 A g<sup>-1</sup> rates. The discharge capacitances can be obtained by following equation [14]:

$$C = \frac{q}{\Delta V \times m} = \frac{\int i\Delta t}{\Delta V \times m}$$
(3)

where 'C' is the capacitance (Fg<sup>-1</sup>), 'q' is the total charge, ' $\Delta V$ ' is the voltage change, 'm' is the mass of the active materials in both electrodes, 'i' is the current, and 't' is time. Also, the I-R drop can be calculated by the following equation [15]:

$$R = \frac{V_{charge} - V_{discharge}}{2I} \tag{4}$$

where ' $V_{charge}$ ' is the voltage of the cell at the end charge, ' $V_{discharge}$ ' is the voltage of the cell at the starting discharge and 'I' is the absolute value of the charge/discharge current. The IR drops of LTO and urchin-like TiO<sub>2</sub> are 0.2 and 0.028  $\Omega$ , at 0.5 A g<sup>-1</sup> rates. It can be elucidated by high theoretical capacity and modification in morphology of urchin-like TiO<sub>2</sub>.

For the more understanding about electrochemical performance of hybrid supercapacitors, the cyclic voltammogram (CV) curves of the hybrid supercapacitors using LTO and urchin-like  $TiO_2$  anode are shown in Fig. 2(b). The polarization values and gross areas from CV curves are valuable to understand electrochemical performance of hybrid supercapacitors. Both samples show the different polarization values derived from between anodic and cathodic peak, indicating reversibility [16]. The polarization can be expressed as [16, 17]:



Fig. 2. (a) Initial charge-discharge curves and (b) cyclic voltammogram curves of hybrid supercapacitors using LTO and urchin-like TiO<sub>2</sub>.

$$\Delta \varphi = (\varphi_a - \varphi_c)/V \tag{5}$$

where ' $\varphi_a$ ' is the anodic peak, ' $\varphi_c$ ' is the cathodic peak, and ' $\Delta \varphi$ ' is the difference between the anodic and cathodic peak potentials. The polarization values of LTO and urchin-like TiO<sub>2</sub> are 770 and 310 mV, respectively. Based on the result, we can infer that urchin-like TiO<sub>2</sub> has a remarkable advantage of smooth Li ion transfer. Furthermore, urchin-like TiO<sub>2</sub> shows larger gross areas, indicating degree of electrochemical reactions, proportional to the initial discharge capacitances.

Figure 3(a) shows the rate capabilities of hybrid supercapacitors using LTO and urchin-like TiO2 anode. When current density is increased from 0.1 to 3 A g<sup>-</sup> both retentions of hybrid supercapacitors were declined regardless of anode materials. At low current density (below 1 A  $g^{-1}$ ), the retention of hybrid supercapacitor using LTO shows a superior retention than that of urchin-like TiO<sub>2</sub>. However, the urchin-like TiO<sub>2</sub> realizes superior rate capabilities at high current density (above  $2 \text{ A g}^{-1}$ ). Considering the high speed operation of actual hybrid supercapacitors, the urchin-like  $TiO_2$  can be regarded as a suitable anode. The retentions of hybrid supercapactiors using LTO and urchin-like TiO2 were about 48 and 67% at 3 A  $g^{-1}$ . The reason for this seems to be the TiO<sub>2</sub> polymorph, resulting in faster Liion kinetics and higher reversibility [18, 19].

The cycle performances of hybrid supercapactiors using LTO and urchin-like  $TiO_2$  are shown in Fig. 3(b). The cyclability were conducted to compare the longterm degradation of hybrid supercapacitors at 3 A  $g^{-1}$ . Both hybrid supercapacitors have the almost flat lines. Among them, the hybrid supercapacitor using LTO shows the extraordinary cycle performance throughout the whole cycle. However, urchin-like TiO<sub>2</sub> also shows the stable behavior under the same condition. Because cyclability of urchin-like TiO<sub>2</sub> can be improved due to effect of modified TiO<sub>2</sub> which leads to large electrolyteelectrode contact area for the Li ion and electron [20]. Also, the structural deformation is reduced during Li ion insertion/extraction. The capacitance retentions of hybrid supercapacitors using LTO and urchin-like TiO<sub>2</sub> were about 95.9 and 93.6% after 1000 cycles. Therefore, we can conclude that the urchin-like TiO<sub>2</sub> can be deemed to sufficiently comparable in cycle performance to that of LTO [20].

In order to prove superiority of urchin-like TiO<sub>2</sub>, the EIS tests were conducted after charging at 2.8 V, as shown in Fig. 3(c). It is well known that charge-transfer resistance ( $R_{ct}$ ) is one of the most important factor for the cycle performance. The  $R_{ct}$  of urchin-like TiO<sub>2</sub> is relatively low due to reduction of the transport path for Li<sup>+</sup> and electrons. This means that the large active area affects to improve conductivity by electrolyte wetting in electrode. The  $R_{ct}$  values of hybrid supercapacitors using LTO and urchin-like TiO<sub>2</sub> were approximately 0.09 and 0.03  $\Omega$ . The diffusion coefficient of Li-ions (D<sub>Li</sub>) can be also calculated according to in the following equation [21]:

$$D_{Li} = \frac{1}{2} \left( \frac{RT}{An^2 F^2 C \sigma} \right) \tag{6}$$

where '*R*' is the gas constant, '*T*' is the absolute temperature, '*A*' is the surface area of the negative electrode, '*n*' is the number of electrons, '*F*' is the Faraday's constant, '*C*' is the concentration of Li<sup>+</sup>, and ' $\sigma$ ' is the Warburg impedance coefficient. The D<sub>Li</sub> values of hybrid supercapacitors using LTO and urchin-like TiO<sub>2</sub> were and  $1.632 \times 10^{-9}$  and  $8.34 \times 10^{-7}$  cm<sup>2</sup> s<sup>-1</sup>. It can be affected by favorable Li ion conductivity derived from easy insertion and extraction process.

The Ragone plot of hybrid supercapacitors using LTO and urchin-like  $TiO_2$  is shown in Fig. 4. The energy densities (*E*) and power densities (*P*) can be calculated as follows [22, 23]:

$$P = \Delta E \times i/m \tag{7}$$

$$E = P \times t/3600 \tag{8}$$

$$\Delta E = (E_{max} + E_{min})/2 \tag{9}$$

where ' $E_{max}$ ' is the potential at the starting discharge, ' $E_{min}$ ' is the potential at the end discharge, 'I' is the charge and discharge currents, 'm' is the mass of active materials including both the anode and cathode, and 't' is the discharge time in the hybrid supercapacitors. The urchin-like TiO<sub>2</sub> has a maximum energy density of



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Fig. 3. (a) Rate abilities, (b) cycling performances and (c) EIS tests of hybrid supercapacitors using LTO and urchin-like TiO<sub>2</sub>.



Fig. 4. Ragone plot of hybrid supercapacitors using LTO and urchin-like  ${\rm TiO}_2$ .

50.648 Wh kg<sup>-1</sup> at a power density of 194.412 W kg<sup>-1</sup>. It also shows a maximum power density of 12224.356 W kg<sup>-1</sup> at an energy density of 10.134 Wh kg<sup>-1</sup>, exhibiting higher values than those of LTO. The superiority of electrochemical performance of urchin-like TiO<sub>2</sub> was improved by not only high theoretical capacity but also structural stability.

## Conclusions

In this paper, we fabricated cylindrical hybrid supercapacitors composed of activated carbon as a cathode and urchin-like  $TiO_2$  as an anode. From structural properties, the urchin-like  $TiO_2$  show good crystallinity and dense structure composed of numerous nanorods. The superior electrochemical performances of urchinlike  $TiO_2$  can be explained by two main reasons. 1) high surface areas improve the Li ion and electron kinetics 2) excellent structural stability due to suppression of lattice strain. As a result, urchin-like  $TiO_2$  anode presents extraordinary electrochemical performance compared to a  $Li_4Ti_5O_{12}$ . It deserves the promising anode material for high grade hybrid supercapacitors.

#### Acknowledgments

This work was supported by the Industrial Fundamental Technology Development Program (10052745, Development of nano-sized (100 nm) manganese ceramic material for high voltage pseudo-capacitor) funded by the Ministry of Trade, Industry and Energy (MOTIE) of Korea. This work was supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea (No. 20162220100050, No. 20161120100350), in part by The Leading Human Resource Training Program of Regional Neo industry through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and future Planning (NRF-2016H1D5A1910564), and in part by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2016R1D1A3B0393 1927).

## References

- S.H. Lee, H.K. Kim, Y.S. Yun, J.R. Yoon, S.G. Lee, and Y.H. Lee, International Journal of Hydrogen Energy 39 (2014) 16569.
- X. Wang, C. Yan, J. Yan, A. Sumboja, and P.S. Lee, Nano Energy 11 (2015) 765.
- D. Rastler, Electronic Power Research Institute, California, 2009.
- 4. P. Harrop and H. Zervos, ID Tech. Ex., Cambridge, Massachusetts, 2009.
- K. Naoi, S. Ishimoto, J. Miyamoto, and W. Naoi, Energy Environ. Sci. 5 (2012) 9363.
- J. Akimoto, K. Chiba, N. Kijima, H. Hayakawa, S. Hayashi, Y. Gotoh, Y. Idemoto, J. Electrochem. Soc. 158 (2011) A546.
- 7. Y. Ren, Z. Liu, F. Pourpoint, A.R. Armstrong, C.P. Grey, and P.G. Bruce, Angew. Chem. 27 (2012) 2164.
- Y. Wang, B.M. Smarsly, and I. Djerdj, Chem. Mater. 22 (2010) 6624.
- K. Fan, T. Peng, J. Chen, X. Zhang, and R. Li, J. Power Sources 222 (2013) 38.
- W. Guo, C. Xu, X. Wang, S. Wang, C. Pan, C. Lin, and Z.L. Wang, J. Am. Chem. Soc. 134 (2012) 4437.
- E. Hosono, S. Fujihara, K. Kakiuchi, and H. Imai, J. Am. Chem. Soc. 126 (2004) 7790.
- P.J. Pomonis, D.E. Petrakis, A.K. Ladavos, K.M. Kolonia, G.S. Armatas, S.D. Sklari, P.C. Dragani, A. Zarlaha, V.N. Stathopoulos, ad A.T. Sdoukos, Mesoporous. Mater. 69 (2004) 97.
- 13. G.Fagerlund, Matériaux et Construction, 6 (1973) 239.
- 14. J.H. Lee, H.K. Kim, E. Baek, M. Pecht, S.H. Lee, and Y.H. Lee, J. Power Sources 301 (2016) 348.
- S.H. Lee, S.G. Lee, J.R. Yoon, and H.K. Kim, J. Power Sources 273 (2015) 839.
- H. Zhao, Y. Li, Z. Zhu, J. Lin, Z. Tian, and R. Wang, Electrochim. Acta 53 (2008) 7079.
- 17. H.K. Kim and S.H. Lee, Energy 109 (2016) 506.
- 18. Y. Cai, H.E. Wang, J. Jin, S.Z. Huang, Y. Yu, Y. Li, S.P. Feng, and B.L. Su, Chem. Eng. J. 281 (2015) 844.
- J. Ye, W. Liu, J. Cai, S. Chen, X. Zhao, H. Zhou, and L. Qi, J. Am. Chem. Soc. 133 (2011) 933.
- 20. S. Zhao, T. Liua, D. Houa, W. Zenga, B. Miao, S. Hussain, X. Peng, and M.S. Javed, Appl. Surf. Sci. 356 (2015) 259.
- V.H. Nguyen and H.B. Gu, Transactions on Electrical and Electronic Materials 17 (2016) 139.
- 22. J.Y. Luo and Y.Y. Xia, J. Power Sources 186 (2009) 224.
- 23. J.R. Yoon, E. Baek, H.K. Kim, M. Pecht, and S.H. Lee, Carbon 101 (2016) 9.