Novel Hybrid Capacitor Composing a Hollow Titania Nanosphere Anode and a KS-6 Cathode

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Abstract. A full cell has been developed using KS-6 and hollow titania nanosphere as cathode and anode materials, respectively, by using 1:1 weight ratio of cathode to anode materials. Thus developed energy storage system exhibits enhanced voltage up to 5.3 V vs. lithium without causing any safety issues. Since the anode is free from lithium deposition the safety of this energy storing device is expected to be very high. The charge/discharge mechanism of the present system exclusively based on intercalation and de-intercalation of PF_6^- anion at the cathode (KS-6) and Li^+ cation at the anode (hollow titania nanosphere) materials, respectively. In addition, hollow titania spherical structure enhances the rate performance of the device.

Keywords: Hollow titania anode, Graphite cathode, Ion intercalation, Safely of device

1. Introduction

In response to the need for better energy storage devices, lithium ion batteries (LIBs) and electric double layer capacitors (EDLCs) have attracted growing attention [1-3]. To overcome some of the disadvantages encountered presently, we have developed a novel high energy density capacitor called the Megalo-capacitance capacitor, in which graphite positive and activated carbon negative electrodes have been used in combination with Li-free electrolytes [4-5]. Such a mechanism enables us to increase both the capacitance and the working voltage simultaneously. As a result, the energy density of the capacitor is remarkably improved.

Recently, we have developed a full cell using graphite cathode and metal oxide anodes which improves the energy density of hybrid type of capacitors because the charge storage mechanism at the positive graphite material is principally concerned with adsorption and the intercalation of anions into the graphite positive electrode [6-9]. This results in a significant increase of the overall energy density due to the increase in the working voltage and the high energy density of the negative electrode. In this paper, we describe a new energy storage system with a high energy density which is composed of a KS-6 cathode and a hollow titania nanosphere anode.

2. Experimental

The fabrication of hollow titania nanospheres with micelles of poly(styrene-*b*-acrylic acid-*b*-ethylene oxide (PS–*b*–PAA–*b*–PEO) using titanium(IV)butoxide (TBOT) as titanium precursor was carried out as follows. Polymeric micelles solution was prepared by dissolving the required amount of the above polymer in distilled water and then transferred to a volumetric flask to obtain a stock solution with a concentration of 0.5 gL^{-1}. The micelle solution was adjusted to pH 9 by using dilute NaOH. The micelle solution (10 mL) containing NH_3 (20 μL) was stirred for a few minutes followed by addition of desired amounts of TBOT

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(TBOT/PAA = 3 to 8) under vigorous stirring. The milky suspension was stirred at room temperature for an hour and aged at 90 ℃ for 48 h under static conditions. The composite particles were repeatedly washed with distilled water and ethanol and dried at 60 ℃. In order to remove the polymeric template as well as to crystallize the shell wall, the composite particles were heated to 500 ℃ for 3 h in a muffle furnace under air.The artificial graphite KS-6 (Timcal. Co. Ltd., Switzerland) was used for cathode material and laboratory made hollow titania nanosphere was used as anode material to develop a novel energy storage system. Powder X-ray diffraction (XRD, MINIFlex Ⅱ, Rigaku, Japan) using CuK_α radiation. The electrochemical characterizations were performed using a CR2032 coin-type cell. The electrodes were pressed under a pressure of 300 kgcm^{-2} and dried at 160 ^{o}C for 4 h in an oven. The positive and negative electrodes were separated by three glass fiber filter and the amount of the electrolyte was ca. 0.5 mL. The electrolyte was 1M LiPF$_6$-EC:DMC (1:2 by volume) supplied by Ube Chemicals Co., Ltd., Japan. Mass loading of electrodes was 4-6 mg/cm^2.

3. Results and Discussion
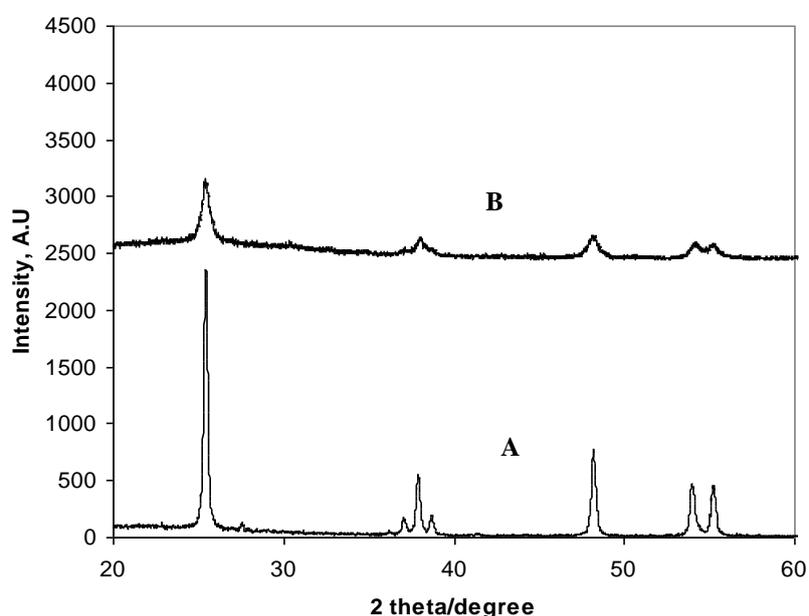
Figure 1. Wide-angle XRD patterns of: (A) bulk titania and (B) hollow titania nanospheres

Comparison of wide-angle X-ray diffraction (WXRD) patterns of nanospheres and bulk titania was shown in Figure 1. The XRD diffraction peak width is often related to the size of particles; the broadening of diffraction peaks of hollow titania spheres indeed indicates a typical nanosized particles. The high-resolution transmission electron microscope (HRTEM, not shown) allows the resolution of lattice fringes of the crystals to be correlated to the (101) planes of the anatase titania. Furthermore, energy-dispersive X-ray spectroscopy spectrum (EDX, not shown) shows strong peaks for titanium and oxygen suggestive of the titania phase. The above results confirm that the titania hollow nanospheres comprised of highly pure anatase titania.
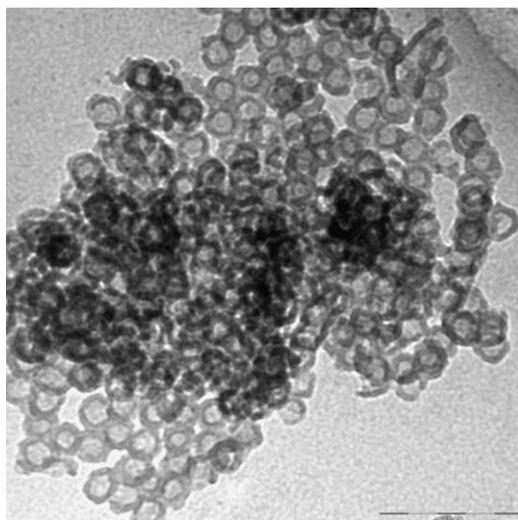
Figure 2. TEM image ofhollow titania nanospheres

The morphology and other physical properties were obtained from transmission electron microscope (TEM). Figure 2 exhibits TEM image of material with TBOT/PAA mole ratio of 5. The average particle size and void space diameter were found to be 28 ± 1 and 16 ± 1 nm, respectively. The wall thickness estimated by TEM (Figure 2) was approximately 6 ± 1 nm. However, at lower TBOT/PAA ratios, the degree of aggregation of nanospheres is quite low compared to TBOT/PAA 8 (not shown), due to deposition of titania species outside micelle domain. Furthermore, the PS block core size estimated from the TEM observation was found to be 23 ± 1 nm; however, after calcinations the void space diameter was approximately 16 ± 1 nm due to shrinkage. The total pore volume and BET surface area of hollow titania nanospheres were found to be 0.59 cm^3g^{-1} and 189 m^2g^{-1}, respectively.
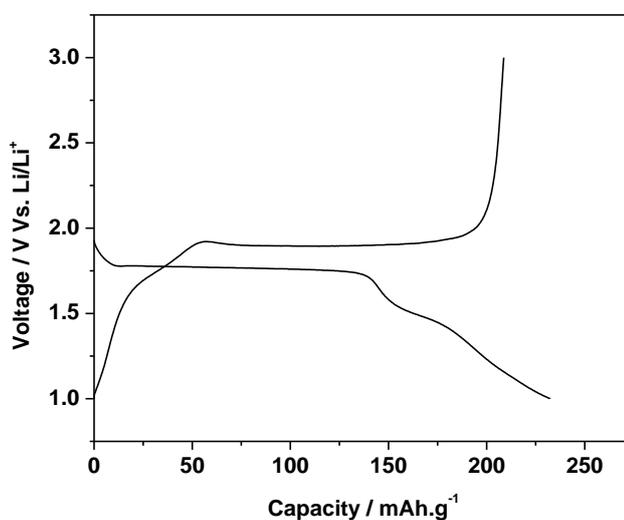

Figure-3 The initial charge/discharge curves for the hollow titania nanosphere/Li half-cell in the voltage range of 3.0-1.0 V at a current density of 100 mAg^{-1}.

Figure 3 exhibits the discharge/charge voltage profiles for first and second cycles at a 0.25 C rate with a voltage window of 1.0–3.0 V vs. Li/Li+. Interestingly, the first charge and discharge capacities are found to be 232.8 and 208.2 mA h g^{-1}, respectively, corresponding to a nominal insertion coefficient of x = 0.62, which exceeds the theoretical capacity of anatase TiO_2. The higher insertion coefficient may be attributed to unique behavior of tiny hollow nanospheres with a thin shell having high surface area which favors surface-confined charge storage. The coulombic efficiency of the first cycle is 87%. Thus, the observed results prove that the hollow titania nanospheres not only overcome the irreversible capacity loss during the first cycle but also show an improved Li insertion coefficient of 0.62 due to extra lithium storage in void space.
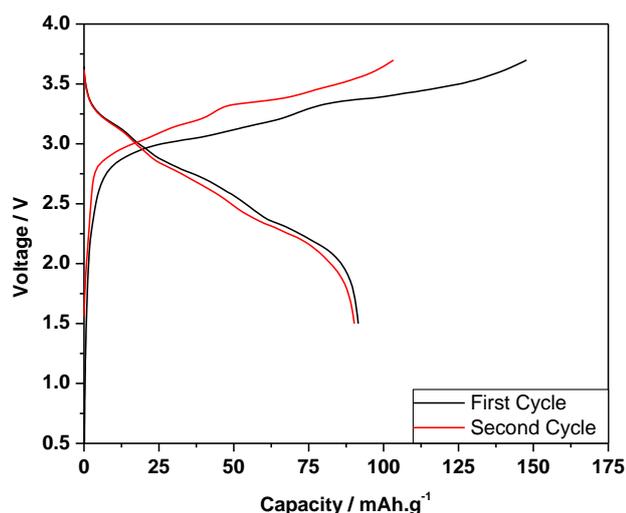
Figure-4 The initial charge/discharge curves for the KS-6/hollow titania nanosphere cell in the voltage range of 4.0-1.5 V at a current density of 100 mAg^{-1}.

Figure–4 shows the first and second charge/discharge curves of the KS-6/hollow titania nanosphere energy storage system. The initial charge and discharge capacities of the cell are 185 and 93 mAh g^{-1}, respectively. The low coulombic efficiency in the first cycles could be attributed to the irreversible capacity associated with anion intercalation into the graphite and its partial exfoliation. However, during the second and subsequent cycles this irreversible capacity loss became smaller. Since the charge/discharge curves are not flat, the average voltage and energy density of this device was calculated by integrating the area under the capacity/voltage profile. The average working voltage of this device is 2.92 V, which is significantly higher than other hybrid capacitors. According to the total weight of active materials in the voltage region of 1.0–4.0 V, this cell delivers 134 Wh Kg^{-1} as energy density. Therefore, the energy density of this device is much higher than that of Megalo-capacitance capacitors and AC/TiO$_2$ type hybrid capacitors [11].
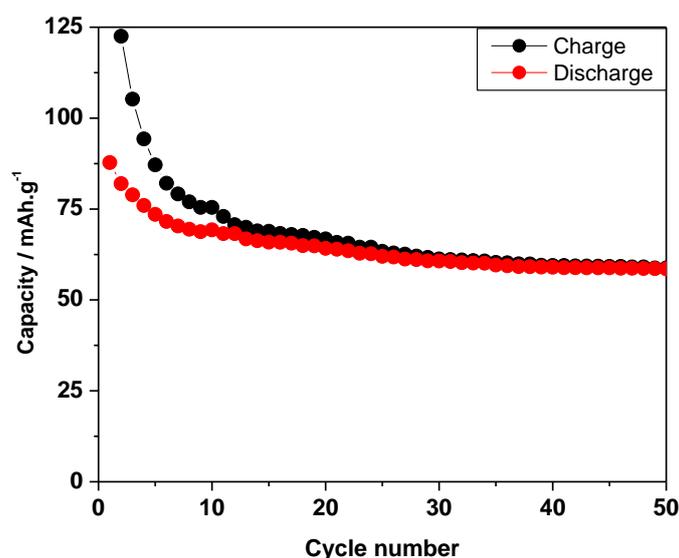

Figure-5 The initial charge/discharge curves for the hollow titania nanosphere/Li half-cell in the voltage range of 4.0-1.5 V at a current density of 100 mAg^{-1}.

Figure-5 exhibits charge/discharge capacities versus the cycle number of KS-6/ hollow titania nanosphere full cell. The charge/discharge capacities decrease for first few cycles due to electrolyte

decomposition on the graphite cathode and surface film formation on the anode. The capacity retention from 10th cycle to 50th cycle is about 93 %.
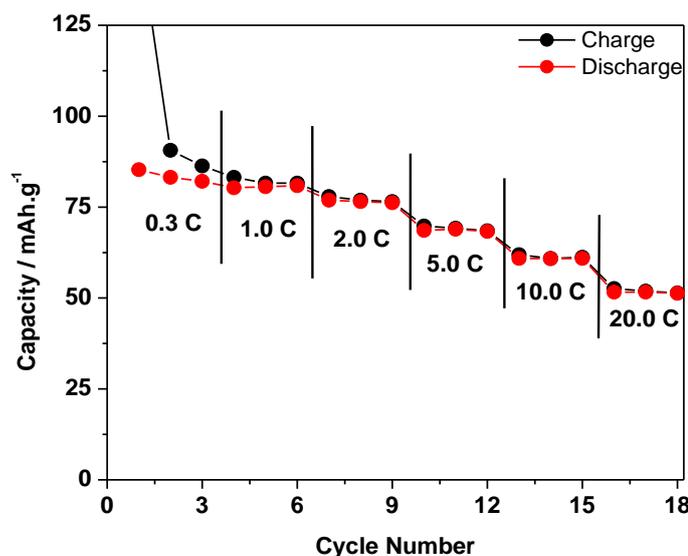

Figure-6 The rate performance of the KS-6/ hollow titania nanosphere cell in the voltage range of 4.0-1.5 V at different current densities.

Figure 6 exhibits the rate capabilities of KS-6/ hollow titania nanosphere with mass ratio of 1:1 in the voltage range of 1.5–4.0 V. At 0.3 C rate it delivers 88.9 mAh g^{-1}. As shown in figure 6, when the charge/discharge rate increases, the specific capacities decrease gradually. At 20 C rate its discharge capacity is 54.54 mAh g^{-1}. However, even at such a high rate the energy density of KS-6/hollow titania nanosphere is still higher than EDLCs owing to the higher charging voltage and larger capacity of the working electrodes.

As we noted, when this cell is charged to 3.5 V, PF_6^- intercalates into KS-6 and Li^+ inserts into titania hollow nanospheres. In typical LIBs, solvation and de-solvation reactions accompanied when Li-ion is intercalated or de-intercalated into metal oxide positive electrodes. This causes deterioration of the cycle life in LIBs and the charging voltage is limited to roughly 4.3 V vs. Li/Li$^+$. Since PF_6^- does not have solvation or de-solvation effects, the potential of the graphite based cathode could be raised up to 5.3 V vs. Li/Li$^+$ without any safety issues or deterioration in the cycle life of the cell. In the device, when the KS-6/TiO$_2$ cell is discharged, the Li^+ and PF_6^- ions are extracted from their respective electrode structures and reconstitute the original LiPF$_6$ electrolyte solution. This phenomena can be easily observed by the (0 0 2) peak shifts in XRD spectra in KS-6 electrode. This was due to anion intercalation into graphene layers of the KS-6 which is also in good agreement with the literature [12–15].

4. Acknowledgment

5. References

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