

A Novel Hybrid Supercapacitor Using a Graphite Cathode and a Niobium(V) Oxide Anode

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To meet the high current load requirement from the high energy density realized by metal oxide and high power density graphite, we propose a novel hybrid supercapacitor consisting of Nb₂O₅ and KS6 graphite in 1.0 M LiPF₆-EC:DEC (1:2). This new system exhibits a sloping voltage profile from 2.7 to 3.5 V during charging and presents a high operating voltage plateau between 1.5 and 3.5 V during discharging. The cell was tested at a current density of 100 mA/g with a cut-off voltage between 3.0 and 1.0 V. This novel energy storage system delivers the highest initial discharge capacity of 55 mAh/g and exhibits a good cycle performance.

Key Words: Novel energy storage system, Graphite, Niobium(V) oxide, Intercalation/de-intercalation

Introduction

Recently, supercapacitors have drawn extensive attraction to meet the increasing demand for energy storage with high power and long durability. Using activated carbon as positive and negative electrodes in electric double-layer capacitors (EDLCs) inevitably restricts their functional ranges, such as specific capacitance, working voltage, and energy density, even though they possess the advantage of long cycle life and high power density.^{1,2} Hence, research efforts are underway to improve the energy density of EDLCs. Hybrid supercapacitors with metal oxides and activated carbon as positive and negative electrodes are one of the ways to increase the energy density of EDLCs. In a supercapacitor, two symmetric capacitors are connected in series and the total capacitance is halved:

$$1/C_{\text{total}} = 1/C + 1/C$$

$$C_{\text{total}} = C/2$$

However, in a hybrid supercapacitor, a battery electrode replaces one of the electrodes. This electrode accumulates the charge through a faradaic electrochemical process (redox reaction) that not only increases the specific capacitance of the capacitor, but also extends the working voltage. As a result, the energy density of the capacitor is enlarged considerably. Therefore, we can achieve total capacitance of the single capacitor electrode with the added advantages of the battery electrode.³ In a hybrid supercapacitor, the positive electrode stores charge in a reversible non-faradaic reaction of anions on the surface of activated carbon material, whereas a reversible faradaic reaction occurs at the negative metal oxide electrode. This new, state-of-the-art hybrid supercapacitor technology shows increased energy density, excellent cycle life, and high working voltage. Although hydrous RuO₂ displays superior properties with respect to specific capacitance, cycling stability, and conductance, the cost is too high. However, niobium(V) oxide is one of the cheapest materials

used as a metal oxide in lithium secondary batteries as it has extremely high chemical stability. N. Kumagai *et al.* have reported the structural and electrochemical properties of niobium(V) oxide for rechargeable lithium batteries.^{4,5} But for the first time, we present here the application of niobium(V) oxide as electrode material for hybrid supercapacitor.

Graphitic carbon materials are the current materials of choice for the negative electrode in commercial lithium-ion batteries. Among these graphitic carbons, highly graphitized materials are particularly attractive due to their high, reversible specific charge up to 372 mAh/g, good cycling stability, and high electronic conductivity. Usually, graphite is not a capacitor material because of its small ability of adsorption. It can, however, absorb anions in non-aqueous solutions if activated carbon is used as the counter electrode. The formation of an efficient passivation film of the graphite particle surface during the first electrochemical reduction is essential for the proper functioning of these electrode materials. The storage capacity of graphite is further increased by means of adjusting the comparative weight ratio of the activated carbon electrode. Recently, Yoshio *et al.* reported that graphite can be used as a suitable positive electrode material for high-energy electrochemical capacitors.⁶⁻⁸

In this communication, we introduce a novel hybrid capacitor with a high energy density, in which a graphite electrode with a small surface area was chosen as a positive electrode and niobium oxide as a negative electrode. The electrochemical characterization of this novel energy storage system was studied by galvanostatic charge-discharge testing.

Experimental

The artificial graphite KS6 (Timcal Co. Ltd., Switzerland) was used for the cathode material and commercial Nb₂O₅ (Wako Co. Ltd., Japan) was used as anode material. Powder X-ray diffraction (XRD, MINIFlex II, Rigaku, Japan) using CuK α radiation was employed to identify the intercalation of

anions and structural changes in positive and negative electrodes during charge/discharge cycling. Electrochemical characterizations were performed using a CR2032 coin-type cell. To investigate the electrochemical properties of the KS6 positive material, a half cell was fabricated with 10.0 mg of accurately weighed active material and 6.0 mg of conductive binder (4.0 mg of Teflonized acetylene black (TAB) and 2.0 mg of graphite). It was pressed onto 200 mm² stainless steel mesh under a pressure of 300 kgcm⁻² and dried at 160 °C for 4 h in an oven. The cathode and anode were each fabricated with a 1:1 weight ratio of cathode to anode, using 10.0 mg of accurately weighed active material and 6.0 mg of conductive binder with the electrodes separated by a glass fiber filter.

The charge/discharge current density was 100 mA/g with various cut-off voltages (0 - 3.5 V, 1.5 - 3.5 V, and 2.0 - 3.5 V) at 25 °C. All electrolytes used in this study were a mixture of 1.0 M LiPF₆-ethylene carbonate (EC): diethyl carbonate (DEC) (1:2 by vol., Ube Chemicals, Japan).

Results and Discussion

In our previous reports, we studied several types of nano-storage carbons and found the commercial KS6 graphitic carbon to be one of the better nano-storage carbons.^{6,7} The KS6 belongs to Franklin's definition of graphite because the value of the interlayer distance, $d_{(002)}$, is less than 3.36 Å (Fig. 1). The intensity of the (002) peak of KS6 is not as high as natural graphite. The KS6 has an average particle size of 6.0 μm and a specific surface area of 18.0 m²/g. The electrochemical properties of KS6 as anode material in the lithium secondary battery have been studied previously.^{9,10} Niobium(V) oxide is known to have a number of different structural modifications. Among the several structures of Nb₂O₅, the orthorhombic structure exhibits good capacity owing to a reversible structural change during the charge and discharge process. The Nb₂O₅ used in this study has an orthorhombic structure with a lattice parameter of $a = 6.05$ Å, $b = 29.04$ Å, and $c = 3.86$ Å (JCPDS card #27-1003). In Fig. 1(b), the Nb₂O₅ spectrum reveals a high degree of crystallinity and larger particle sizes.

Figure 2 shows the initial charge/discharge curves for the KS6/Nb₂O₅ with an electrode mass ratio of 1:1 at a current density of 100 mA/g at various cut-off voltages, namely 3.5 - 0 V, 3.5 - 1.5 V, and 3.5 - 2.0 V. It clearly shows a curved line with two linear regions. The cell voltage increases suddenly up to 2.7 V during the first charging and then gradually increases up to 3.5 V. The discharge capacity was small when the charges increased to 2.7 V as the amount of anion adsorption to the edge plane regions of the graphite was not large. Since the anion is intercalating between the graphite layers during the voltage increases from 2.7 to 3.5 V, the discharge capacity increases. The discharge capacities of KS6/1.0 M LiPF₆-EC:DEC(1:2)/Nb₂O₅ cells were 55, 48, and 45 mAh/g, respectively. This novel energy storage system has a high energy density due to a high working voltage (3.5 V) that is greater than the carbon-graphite, megalo capacitance capacitor (2.75 V).

Figure 3 shows the variation in specific discharge capacity

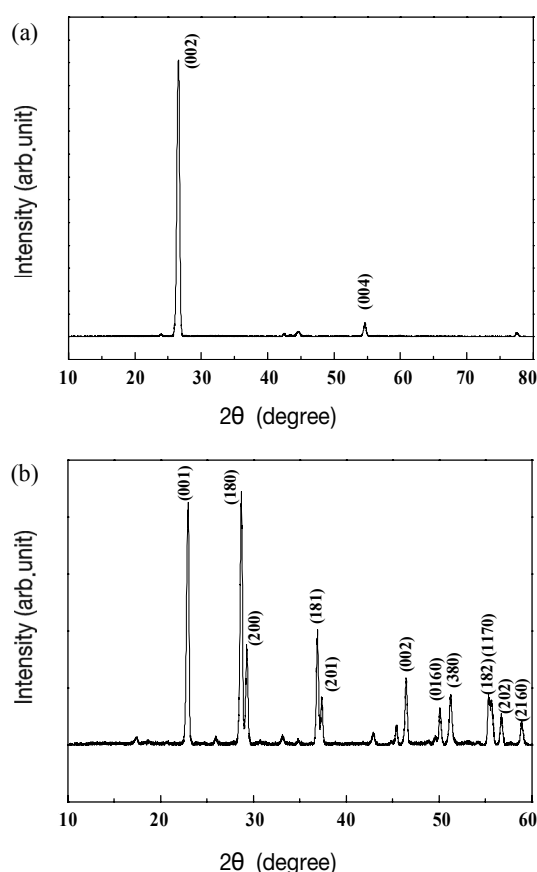


Figure 1. XRD patterns of (a) KS6 and (b) Nb₂O₅.

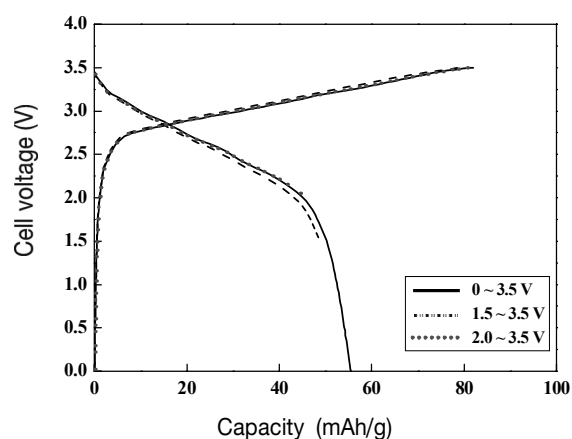


Figure 2. The initial charge/discharge curves for the KS6/1.0 M LiPF₆-EC:DEC (1:2)/Nb₂O₅ with an electrode mass ratio of 1:1.

with the number of cycles for the KS6/1.0 M LiPF₆-EC:DEC (1:2)/Nb₂O₅ energy storage system. The discharge capacity of this cell at cut-off voltages 3.5 - 0 V decreased to 30 mAh/g after 20 cycles and showed poor cycle retention of 54% after the 50th cycle. This may be due to the degradation of graphite volume when the PF₆⁻ ions had completely intercalated and de-intercalated between the graphite layers. The PF₆⁻ ions still remained in the interlayer spaces of the graphite even after discharging to 1.5 V. This destroyed the graphite structure and caused a decreased cycleability in the energy storage system.^{11,12}

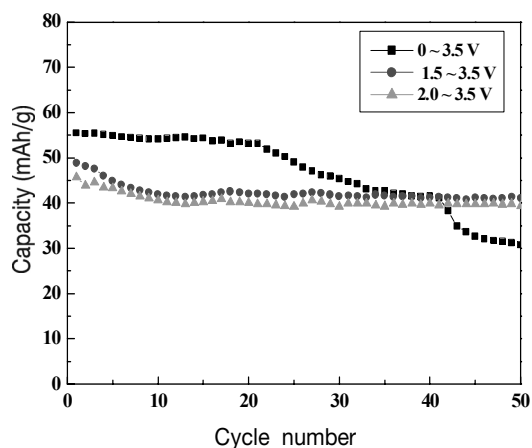


Figure 3. Specific discharge capacity vs. cycle number for the KS6/1.0 M LiPF₆-EC:DEC(1:2)/Nb₂O₅ system at a current density of 100 mA g⁻¹s.

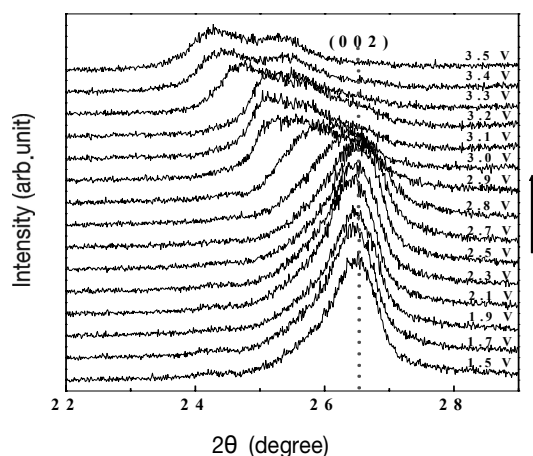


Figure 4. *In-situ* XRD patterns of the KS6 (graphite) electrode during the first charging process of the KS6/Nb₂O₅ energy storage system for KS6 to Nb₂O₅.

From this figure, it proves that the cell has the best performance in terms of capacity and cycle retention rate in the voltage region between 3.5 and 1.5 V, avoiding significant damage to the graphite layers.

In order to investigate the reaction mechanisms and structural changes occurring at the KS6 cathode material, *in-situ* XRD analysis was conducted at various voltage regions. As shown in Fig. 4, the (002) peak at 26.5° indicates a well-ordered graphitic structure. At 2.9 V, the peak shifted to a lower angle and split into two peaks of 24.3° and 25.3° in the 3.5 V regions. The (002) peak disappeared when the voltage reached 3.5 V, due to the insertion and accumulation of PF₆⁻ ions within the interlayer spaces of the KS6 electrode. From the *in-situ* XRD diffraction, we found two unique peaks at 24.3° and 25.3° when the cell was charged to 3.5 V. From the Bragg equation, the 'd' value of these peaks were 3.73 and 3.58 Å, respectively. A more detailed discussion regarding the *in-situ* XRD measurements conducted in the Nb₂O₅ electrode during charging and the electrochemical properties of the novel hybrid system will be reported elsewhere.

When the cell was charged, the ions in the LiPF₆ electrolyte solution migrated to their respective electrodes. The PF₆⁻ ions intercalated into the interlayer spaces of the graphite cathode, while the lithium ions intercalated into the structure of Nb₂O₅ electrode. Conversely, when the cell discharged, the lithium ions and PF₆⁻ ions were extracted from their respective electrode structures and reconstituted the original LiPF₆ solution. This type of cell does not fall into any of the existing categories of capacitors or rechargeable batteries. We suggest that the mechanism of this cell is one of a novel energy storage system and that this system has some merits in terms of safety and high energy density compared with the Li-ion battery and EDLC, respectively. In this system, the safety of an energy storage system can be remarkably improved by the replacement of graphite with Nb₂O₅ for the anode. In general, the lithium ions intercalated into a carbon anode can induce a reaction with the electrolyte, resulting in the decomposition of the cathode material and the release of free oxygen. Furthermore, cell shorting can easily occur due to lithium deposition on the surfaces of the carbon. However, in this novel energy storage system insertion of lithium ions from the electrolyte into the Nb₂O₅ structure can be suppressed because metal oxides have lower conductivity than graphite and Nb₂O₅ also has a higher intercalation voltage with no lithium deposition. We also suggest that this new energy storage system can be improved by optimizing the test conditions. In a previous study,¹³ we reported that the cathode to anode weight ratio was an important factor in improving megal-capacitance capacitors in the terms of high capacity and cycleability. The mechanism of megal-capacitance capacitor function is the adsorption and desorption of the edged plane surface of the graphite in KS6 cathode material when the weight ratio of cathode to anode equals 1:1. We suggest that the controlled weight ratio of cathode to anode in the KS6/Nb₂O₅ energy storage system will improve capacity and cycleability.

Conclusion

For the first time, a novel hybrid system consisting of KS6 graphite and Nb₂O₅ has been tested for suitability as a hybrid supercapacitor. The charge/discharge mechanism of this new system involved the intercalation/de-intercalation of anions at the cathode (graphite) and cations at the anode (Nb₂O₅) materials, respectively, and displays the best electrochemical properties in the voltage region between 1.5 and 3.5 V.

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