Improved performance of cylindrical hybrid supercapacitor using activated carbon/ niobium doped hydrogen titanate

Jeong Hyun Lee [a], Hong-Ki Kim [a], Esther Baek [a], Michael Pecht [b], Seung-Hwan Lee [b, **], Young-Hie Lee [a, *]

[a] Dept. of Electronic Materials Engineering, Kwangwoon University, South Korea
[b] Center for Advanced Life Cycle Engineering, University of Maryland, Room 1103, Building 89, College Park, MD 20742, USA

HIGHLIGHTS

- We fabricated a hybrid supercapacitor using Nb doped $H_2Ti_{12}O_{25}$/activated carbon.
- The HTO was reported to have higher capacity than LTO and TiO_2 (B).
- A hybrid supercapacitor using $H_2Ti_{11.85}Nb_{0.15}O_{25}$ show improved power/energy density.

ARTICLE INFO

ABSTRACT

A cylindrical hybrid supercapacitor is fabricated using activated carbon positive electrode and $H_2Ti_{12-x}NbxO_{25}$ ($0 \leq x \leq 0.6$) negative electrode materials. The hybrid supercapacitor using $H_2Ti_{11.85}Nb_{0.15}O_{25}$ exhibits the best electrochemical performance. It has a capacitance of 78.4 F g^{-1}, charge transfer resistance (R_{ct}) of 0.03 Ω, capacitance retention of 91.4% after 1000 cycles at 3.0 A g^{-1} and energy density of 24.3 W h kg^{-1} at a power density of 1794.6 W kg^{-1}. Therefore, the Nb doped HTO negative electrode material is a promising candidate as an energy storage system for electric vehicles (EVs).

1. Introduction

The world faces growing environmental and energy issues, such as global warming and declining stocks of oil. One of the ways to resolve these problems is to increase the development and use of alternative energy, such as hydropower, wind and solar energy [1]. However, such energy sources are impractical for use in portable electronic devices and electric vehicles (EVs), and instead, energy storage systems are typically used in such electric devices, and their development is being constantly studied. Among previously used energy storage systems, secondary batteries are problematic when used in EVs because they have low power density (50–200 W kg^{-1}) and short cycle life. Although supercapactior has high power density (<3 kW kg^{-1}), it has the still low energy density reported by Yang et al. (20–50 wh kg^{-1}) [2] and Yang et al. (30–90 W h kg^{-1}) [3] due to physical charge-storage mechanism. So, it is difficult to apply to EVs because of low energy density [4,5]. However, secondary batteries have high energy density (150–200 W h kg^{-1}), and supercapacitors have advantages such as high power density (2–5 k W kg^{-1}), low equivalent series resistance, and long cycle life [5,6]. Thus, hybrid supercapacitors, a new energy storage system that has higher power and energy density, are now being developed for EVs. The hybrid supercapacitor combines the advantages of both supercapacitors and secondary batteries. It is also receiving attention as a non-polluting power source [7] with better performance (high energy-power density and long cycle life) than both secondary batteries and supercapacitors [5]. Various materials, including carbon, oxide, and metal materials, are employed in the negative and positive electrode of hybrid supercapacitors. Among carbon materials, activated carbon is used as a positive electrode

* Corresponding author.
** Corresponding author.
E-mail addresses: inyoungezz@nate.com (S.-H. Lee), yhlee@kw.ac.kr (Y.-H. Lee).

owing to its high surface area, which has the advantage of being able to store charge during BF^{4-} ion adsorption/desorption at its surface [5,8]. There are many promising candidates for negative electrode materials, such as $Li_4Ti_5O_{12}$ (LTO), TiO_2 (B), $H_2Ti_3O_7$ and $H_2Ti_{12}O_{25}$. $H_2Ti_3O_7$, and $H_2Ti_{12}O_{25}$ are an intermediate phase produced during the TiO_2 (B) fabrication [9–13]. Although $H_2Ti_3O_7$ has a higher initial capacitance than LTO, TiO_2 (B), it is difficult to apply as a negative electrode because it has a bad cycle performance [10]. On the other hand, $H_2T_{12}O_{25}$ (HTO) has a flat potential plateau at approximately 1.55 V and a capacity of 236 mAh g^{-1}. Here, the quantity of electric charge for Li$^+$ ion is 26.801 A h by Faraday's law. When a Li$^+$ ion is inserted in a HTO unit cell, the capacity of the inserted Li$^+$ ion per the HTO unit cell is calculated as follows:

$$capacity \ of \ Li^+ \ ion \ per \ HTO \ unit \ cell$$
$$= \frac{quantity \ of \ electric \ charge \ for \ Li^+ \ ion}{HTO \ molecular \ weight} \quad (1)$$

Therefore, the capacity of the inserted Li$^+$ ion per the HTO unit cell is 27.448 mAhg^{-1}, and the inserted Li$^+$ ion can be regarded as approximately 8 per HTO unit cell [14]. In a life cycle evaluation, HTO exhibited a discharge capacity retention of 96% after 50 cycles [9]. HTO also showed higher specific capacity than LTO and TiO_2 (B). Thus, HTO can be applied to the negative electrode of the hybrid supercapacitor because of its superior electrochemical performance. To improve the cycle properties and capacity of HTO as a negative electrode, Nb-doped HTO was studied [15–19]. Shi et al. [15] reported that Nb doping increased electronic conductivity and Li ion diffusion. In this study, a hybrid supercapacitor was fabricated using Nb-doped HTO as a negative electrode and activated carbon as a positive electrode, and the electrochemical performance were investigated.

2. Experimental

The HTO was prepared by a solid-state method. First, in order to prepare Nb-doped HTO, Nb_2O_5 was mixed with TiO_2 in a 0–0.6 M ratio using a ball mill. After drying, the mixture was calcined at 1350 °C for 10 h in air. The precursor $Na_2Ti_{3-x}Nb_3O_7$ was fabricated by mixing Na_2CO_3 and $Ti_{1-x}Nb_xO_2$ (1:3 M ratio). The mixture was sieved in a 250 mesh sieve and heated at 800 °C for 20 h in air. The resultant $Na_2Ti_{3-x}Nb_xO_7$ was transformed to $H_2Ti_{3-x}Nb_3xO_7$ through Na$^+$/H$^+$ ion exchange reaction in 1 M HCl solution over 3 days at 60 °C. The $H_2Ti_{12-x}Nb_xO_{25}$ was prepared by heating as-prepared $H_2Ti_{3-x}Nb_xO_7$ at 300 °C for 5 h in air. The crystal structure of the Nb doped HTO was analyzed by X-ray diffraction (XRD), and its microstructure was observed by field emission scanning electron microscopy (FE-SEM). Electrical conductivities of all samples were measured using the four-point probe measurement (RTS-8 Four-Point probe meter). The hybrid supercapacitor was assembled as a cylindrical cell to measure its electrochemical performance. An activated carbon was used as the positive electrode. For the negative electrode, Nb doped HTO was mixed with conductive carbon black binder (Super P) and polyvinylidone fluoride (PVDF) in the weight ratio 83:7:10 in N-methyl pyrrolidinone (NMP) solvent. The areal loading amount of the total electrode materials is 20 g. The obtained slurry was spread to a thickness of 125 μm on aluminum foil using a bar coater. In order to make a negative electrode of 70–80 μm thickness, the covered aluminum foil was pressed. In an argon-gas-filled glove box, the positive electrode, separator, and negative electrode were assembled as a cylindrical cell. Before being impregnated in an electrolyte solution of 1.5 M $LiBF_4$ (5 g), the cell was dried in a vacuum oven for 48 h to remove the moisture in the cell. Electrochemical measurement was carried out by a programmable multichannel battery tester (Avbin

Instruments).

3. Result and discussion

Fig. 1 shows the XRD patterns of pristine and Nb doped HTO powder. The XRD pattern of the pristine HTO was well formed as previously reported [9]. The XRD patterns of Nb doped HTO show similar shapes to pristine HTO without any secondary phases. All XRD patterns of Nb doped HTO compared with pristine HTO indicated that they were moved as low degree by Bragg's law (nλ = 2dsinθ) because the ion radius of Nb^{5+} (0.69 Å) are bigger than that of Ti^{4+} (0.68 Å) and some of the Ti^{4+} will be changed to Ti^{3+} by Nb doping. This transfer is called "charge compensation", and will increase the lattice parameter of HTO because the ion radius of Ti^{3+} (0.76 Å) is larger than that of Ti^{4+} (0.68 Å) [14–16]. The extended lattice plane spacing by Nb doping, causes smoother and faster kinetics of Li ions. This affects the performance of hybrid supercapacitor as positive effect along with the tunnel structure of HTO [20].

Fig. 2 shows the SEM images of pristine HTO and Nb doped HTO. In comparison with pristine HTO, the particle size of Nb doped HTO was decreased with increasing Nb content. However, the morphology of all powder was similar as shown in Fig. 2. These results indicated that Nb doping affect particle size of HTO [21]. The reduced grain size enables increase the contact area for Li ion diffusion from electrolyte.

Before investigating the electrochemical performance of the hybrid supercapacitor by using various hydrogen titanate oxides as negative electrodes, the hybrid supercapacitors were balanced to obtain excellent electrochemical performance by controlling the electrode thickness [22]. This is related to the fact that the insertion/extraction rate of the HTO negative electrode is slower than the adsorption/desorption rate of the AC positive electrode due to a different electrochemical reaction. Table 1 shows the discharge capacitance retention according to the combination of different electrode thicknesses. At 0.1 A g^{-1}, the initial capacitance is increased by a thick electrode. This is because both electrodes have sufficient time for an electrochemical reaction. However, the capacitance retention is decreased at a high rate. This results can be inferred from the fact that the slower electrochemical reaction of HTO relates to the insertion/extraction of Li$^+$ ion than AC. In other words, as the current density increases, the capacitance retention of hybrid supercapacitors decreases because the entire thickness of the negative electrode cannot sufficiently react with the Li$^+$ ion. Only the upper part of the electrode can be involved in the electrochemical performance. Therefore, the insertion/extraction of the Li$^+$ ion is not significantly responsive inside the HTO structure [23]. In contrast, regardless of current density, the capacitance retention of the AC is increased its AC increases. Although the initial capacitance of the 90–240 μm electrode is the highest at 0.1 A g^{-1}, the electrode does not have optimal capacitance retention due to the low efficiency of the Li$^+$ ion insertion/extraction. Therefore, it can be determined that the 70–240 μm electrode has the optimal electrode thickness, having a capacitance retention of 52% at 3.0 A g^{-1}.

Fig. 3 shows the electrochemical performance under cyclic voltammetry (CV) testing at a scan rate of 10 mV s^{-1} in the potential range between 0 and 2.8 V (working voltage of activated carbon 4.3 V and HTO 1.5 V). The electrochemical Li$^+$ ion insertion/extraction reaction can be observed in the CV curve [18,24]. All CV curves show identical shape, and $H_2Ti_{11.85}Nb_{0.15}O_{25}$ appears to exhibit the best property. However, the phenomenon called "mirror effect" was not observed in the CV curve of the hybrid supercapacitor above 1.5 V. As previously reported, the area up to about 1.5 V was dominated by the AC electrode and the other region was dominated by various negative electrode materials [25]. All cells