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High-energy, fast-charging, long-life lithium-ion batteries using $TiNb_2O_7$ anodes for automotive applications

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HIGHLIGHTS

- Lithium-ion batteries using TNO anodes have been developed for EV applications.
- Electrochemical properties of TNO during lithium storage were studied.
- HD-TNO anodes with carbon coating had high-rate capability and high capacity.
- TNO/NCM batteries exhibited a high energy density and fast-charging.
- Cycle-life was predicted to be 14000 cycles.

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ABSTRACT

Electrochemical properties of $TiNb_2O_7$ (TNO) electrodes during lithium storage have been studied in order to develop an alternative anode with high-capacity, fast-charging, and long-life to $Li_4Ti_5O_{12}$ (LTO) in lithium-ion batteries. High-density TNO (HD-TNO) composite electrode consisting of micro-size spherical TNO secondary particles coated with carbon exhibited high-rate capability, long cycle-life, and a high volumetric capacity of more than twice that of LTO composite anodes. Large-size lithium-ion batteries using the HD-TNO anode and a $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM) cathode with a capacity of 49 A h were fabricated for automotive applications, and were found to have a high energy density of 350 W h L^{-1}, a high input-power density of 10 kW L^{-1} for 10 s at 50% state of charge (SOC), and fast-charging from 0% to 90% SOC in less than 6 min. The capacity retention at 7000 cycles was 86% by full charge-discharge cycling at 1C rate. Cycle life was predicted to be 14000 cycles at 80% capacity retention. It was demonstrated that the TNO/NCM batteries have high energy-density, fast-charging, and long cycle-life for automotive applications such as electric vehicles with long driving ranges by fast-charging.

1. Introduction

Development of large-size lithium-ion batteries for automotive applications such as electric vehicles (EVs) and plug-in hybrid electric vehicles (PHEVs) has focused on enhancement of energy density. However, conventional lithium-ion batteries using graphite anodes have limitations in terms of fast-charging, life, safety, and low-temperature performance, which are important subjects for these applications. In particular, fast-charging performance of a few minutes is a strong requirement for enhancing the convenience and promoting the spread of EVs. Long-life of batteries is also required for reduction of the total cost for long-term using EVs and saving the resource. In terms of safety and life, it is necessary that lithium-ion batteries do not suffer any lithium metal plating on anodes during fast-charging and low-temperature charging even at the end of life. It is well known that $Li_4Ti_5O_{12}$ (LTO) anodes do not undergo lithium metal plating during fast-charging and long-term cycling, which leads to long-life and safety [1,2]. However, LTO anode-based batteries have the disadvantage of low energy density, which is not suitable for automotive applications such as EVs with long driving ranges. Therefore, our group [3,4] and Goodenough's group [5,6] have recently proposed $TiNb_2O_7$ (TNO) with a monoclinic structure as an alternative high-capacity anode material to LTO. It is possible to utilize niobium as a battery material because the abundance of niobium in the Earth's crust is comparable with that of lithium and lead [7]. TNO has a theoretical capacity of 387.6 mAh g^{-1} based on 5 Li insertion per formula unit for electron transfer of Ti^{4+}/Ti^{3+}, Nb^{5+}/Nb^{3+} redox couples. The volumetric theoretical capacity based on the true density of 4.34 g cm^{-3} is calculated to be 1680 mAh

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cm^{-3}, which is twice that of graphite. However, TNO has poor ionic and electronic conductivity in practice. It is necessary to develop TNO composite anodes with good electron-conductive networks and shorter lithium diffusion length in TNO particles in order to enhance the capacity and rate capability for lithium-ion batteries.

TNO nanoparticles [8,9] and microspheres [10,11] have been investigated in terms of capacity, rate capability, and cycle life as anodes for lithium-ion batteries. TNO nanoparticle and microsphere composite electrodes containing large amounts of carbon conductor additives such as ketjen black (KB) or acetylene black (AB) and low loading of the active material have been used for enhancing rate capability and cycle-life. More specially, TNO composite electrodes consisting of 60 wt% porous TNO nanoparticles, 25 wt% carbon conductor, and 15 wt% binder additives with a low loading of 0.8–2 mg cm^{-2} were reported to exhibit a long-life, high-power, and a large reversible capacity of 307 mAh g^{-1} based on the TNO active material [8], but the gravimetric capacity based on TNO composite electrode was a low capacity of 184 mAh g^{-1}. TNO composite electrodes consisting of 75% TNO microspheres, 15% carbon black, and 10% binder have also been found to exhibit high rate capability and long cycle-life [10], but the gravimetric capacity based on the composite electrode at 1 C rate was a low capacity of 194 mAh g^{-1}. Moreover, large amounts of carbon conductor additives in composite electrodes cause low-density electrode and low volumetric capacity. Low-density TNO composite electrodes with a low loading have a high rate capability but significantly decrease the volumetric energy density of battery. Automotive applications for EVs and PHEVs require high volumetric energy density as well as high gravimetric energy density. It is necessary to develop TNO composite anodes with high-density and high loading of active material in order to enhance the volumetric energy density. We have developed high-density TNO (HD-TNO) composite anodes with high volumetric capacity, high rate capability, and long cycle-life for practical lithium-ion batteries. In our investigation of promising TNO particles for the anode, micro-size spherical TNO secondary particles coated with carbon are expected to produce high-density electrodes because the micro-size spherical particles have a high tap density and allow reduction of the amounts of carbon conductor and binder additives. This paper reports on the electrochemical properties and performance of HD-TNO electrodes using micro-size spherical TNO secondary particles and large-size lithium-ion batteries using the HD-TNO anodes for EV applications which need long driving ranges by fast-charging and long-life.

2. Experimental

Micro-size spherical TNO secondary particles were prepared by a solid-state reaction as follows. TiO_2 anatase and niobium (V) pentahydroxide ($Nb(OH)_5$) were mixed and mashed by using a planetary ball mill. The mixture was heated at 1100 °C for 12 h to obtain TNO powder. The obtained sample was characterized as monoclinic $TiNb_2O_7$ by x-ray diffraction (XRD, Rigaku Corporation) with CuKα radiation. The TNO powder was mixed with an aqueous solution of disaccharide, and then the mixture was spray dried to form micro-size spherical. TNO secondary particles in the particle-size range of 5–20 μ m, which was then heated at 700 °C in an argon atmosphere for carbonization. Finally, spherical TNO secondary particles with 2 wt% carbon coating were obtained for use as the TNO anode material in lithium-ion batteries. Fig. 1(a) shows XRD patterns of TNO primary particles with no carbon coating after 1100 °C and TNO secondary particles with carbon coating after 700 °C. The peak positions of both samples correspond to the monoclinic structure of $TiNb_2O_7$ (C2/m) listed the standard powder diffraction file (JCPDS: #77–1374) and other previous reports [5,12]. The intensities of XRD pattern in TNO secondary particles with carbon coating was slightly different from those in TNO primary particles with no carbon coating. We consider that such a small difference is caused by a different arrangement of particles between TNO primary and secondary particles. The prepared samples of TNO primary particles with no carbon coating after 1100 °C and TNO secondary particles with carbon coating after 700 °C were analyzed to check the surface morphologies by field-emission scanning electron microscopy (FESEM, SU9000, Hitachi High-Technologies Corporation) and high-resolution transmission electron microscopy (FRTEM, 9000UHRIII, Hitachi High-Technologies Corporation). The sample of TNO particles with carbon coating was prepared by vapor deposition of RuO_4 to observe a thin carbon layer on TNO particles in TEM images. Fig. 1(b) shows a SEM image of the spherical TNO secondary particles consisting of primary particles with the particle-size of about 1 μm. TNO secondary particles with no carbon coating were also prepared using the spray dried method without the disaccharide in order to compare the electrochemical performance. The spherical secondary particle consists of TNO primary particles with a particle size of about l μm. The BET (Brunauer-Emmett-Teller) specific surface areas of the spherical TNO secondary particles were 3 $m^2 g^{-1}$. Fig. 1 (c) and (d) show TEM images of TNO particles with no carbon coating and carbon coating. TNO particles with carbon coating were covered with a thin carbon layer with a thickness of 0.5–3 nm.

The HD-TNO composite electrodes were prepared from a mixed slurry of 91 wt% TNO powder with 2 wt% carbon coating, 5 wt% graphite conductor, 2 wt% carboxymethylcelluose (CMC) binder, and 2 wt % styrene-butadiene (SBR) binder in an aqueous solution. The slurry was coated onto aluminum foil and then dried. The HD-TNO electrodes were pressed to obtain a high electrode density of 2.7 g cm^{-3}. Low-density TNO (LD-TNO) composite electrodes of 1.9 g cm^{-3} were also prepared from a mixed slurry of 70 wt% TNO powder, 20 wt% AB conductor, 7 wt% CMC binder, and 3 wt% SBR binder in aqueous solution for comparison of electrochemical performance.

Electrochemical measurements were performed by using the HD-TNO electrodes with an active material loading of 4–10 mg cm^{-2} on aluminum foil. Charge (lithium insertion)-discharge (lithium extraction) cycling tests, cyclic voltammetry, open-circuit potential, rate performance, and impedance measurements of the HD-TNO and LD-TNO composite electrodes were carried out using a three-electrode glass cell constructed using composite electrodes (2 × 2 cm), a Li metal chip reference electrode, Li metal counter electrode, glass filter separator, and a 1 M $LiPF_6$ in a mixed ethylene carbonate and diethyl carbonate (DEC) (1:2 b y volume) electrolyte. Open-circuit potentials during lithium insertion and extraction for the HD-TNO composite electrode were measured by galvanostatic charging at 15 mA g^{-1} for 10 min in the open-circuit state for 1 h to 0.7 V vs. Li/Li^+. Values of change in entropy (ΔS) during lithium insertion at 10 mA g^{-1} for 1 h with open-circuit potential for 10 h were also calculated from measurements of the temperature dependence of open-circuit potential in the temperature range of −10 °C to 25 °C. Charge (lithium insertion)-discharge (lithium extraction) potential curves of the HD-TNO and LD-TNO composite electrode were measured by galvanostatic charging at 54 mA g^{-1} down to various charge cut-off potentials between 0.7 and 1.2 V for 10 h and discharging at 54 mA g^{-1} up to 3 V at the first cycle. The TNO composite electrodes were charged by a constant potential between 0.7 and 1.2 V after galvanostatic charging down to various cuff-off potentials. The specific capacities of TNO electrodes were calculated based on the weight of TNO active material in the composite electrodes. Charge-discharge rate tests of the LD-TNO composite electrode and HD-TNO composite electrodes with carbon coating and no coating were carried out between 1 and 3 V at various charge-discharge current rates from 0.2 to 10 C. A 1 C rate corresponds to 270 mA g^{-1}. The volumetric capacities of TNO composite electrodes were calculated based on the volume of the TNO composite electrode. Impedance measurements of the HD-TNO electrodes were carried out at various states of charge (SOC) in the frequency range of 1 × 10^6 to 0.01 Hz. All experiments were carried out at 24 °C–26 °C in a dry atmosphere.

Large-size TNO/$LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM) laminated lithium-ion batteries with a capacity of 49 A h were fabricated in order to evaluate cycle life, fast charging, discharge rate performance, and power