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Rapid charge and discharge property of high capacity lithium ion battery applying three-dimensionally patterned electrode

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HIGHLIGHTS

- 3D-patterned electrodes with various types of line patterns were fabricated.
- The effect of pattern specifications on the electrode performance was evaluated.
- The better rate capability is obtained for the narrower width of electrode line.
- The line height and line space hardly affect the rate capability of electrode.
- The charge-transfer resistances hardly depend on the electrode pattern.

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ABSTRACT

The cells applied with a three-dimensionally (3D) patterned $Li_4Ti_5O_{12}$ (LTO) electrode showed good performance as a rechargeable lithium-ion battery. The 3D-patterned electrode was fabricated with a printing apparatus and has many lined patterns with a high aspect ratio standing in line on a current collector. The cell using 3D-patterned electrode showed much better rate capability than that using a conventional flat electrode. In this research, cyclic voltammetry was carried out to investigate the mechanism realizing the high rates of charging and discharging in 3D-patterned electrode. Various types of line patterns were fabricated for 3D electrode by using LTO electrode slurry, and the influences of basic specifications of electrode structure (the space between two neighboring electrode lines, the height and width of electrode) on the charge and discharge characteristics were evaluated to optimize the electrode pattern. In addition, the electrode performance was discussed from the viewpoints of ohmic resistance and charge-transfer resistance of the cells with 3D-patterned and conventional flat electrodes.

1. Introduction

Lithium-ion battery has higher energy density than other conventional rechargeable batteries, namely the amount of energy that can be stored per unit volume and weight is large [1]. Hence recently, the lithium-ion battery is started to be used for electric vehicles [2]. However, its performance is not still enough in both energy and power densities. Therefore, research and development aiming at higher energy density and higher rate performance of lithium-ion batteries are conducted intensively [3,4]. The rate performance of lithium-ion battery depends on the diffusion rate of lithium-ion, particularly in porous composite anode and cathode. High performance requires high current of electrochemical reactions. In order to promote diffusion of the lithium-ion in the cell, it is focused on to increase the surface area of active material layer and to decrease the diffusion length of lithium-ion between anode and cathode [5–9]. On the other hand, higher energy density requires the higher mass per unit volume of active material in the electrode. However, the diffusion resistance of lithium-ions in the electrode increases with increasing the electrode density. Consequently, it is difficult to achieve both high energy density and high rate performance simultaneously in conventional lithium-ion batteries [10].

We have been focusing on three-dimensionally (3D) integrated electrode structure as one of the effective solutions to realize the high rate performance without sacrificing the energy density of batteries [11–14]. In our previous report, a printing method combined with the manufacturing process of electrode was developed

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aiming at a large scale production of 3D structured electrodes for the upcoming demands in battery development [11]. The cyclic voltammogram of the half cell with 3D $Li_4Ti_5O_{12}$ cathode and lithium metal anode indicated a couple of reversible peaks assignable to the lithiation and delithiation of lithium-ions to $Li_4Ti_5O_{12}$ and from $Li_7Ti_5O_{12}$, suggesting that the 3D-patterned electrode fabricated by the printing apparatus works effectively. Furthermore, it was confirmed that the capacity retention at 5 C for the 3D-patterned electrode was 2.3 times larger than that obtained for a conventional flat electrode. These results strongly support the enhancement of lithium-ion diffusion by 3D patterning of electrode.

In this study, cyclic voltammetry was carried out to investigate the mechanism realizing the high rates of charging and discharging in 3D-patterned electrodes. The interfacial resistance difference between the cells with 3D-patterned and conventional flat electrodes was also analyzed in AC impedance measurement. In addition, the influences of basic specifications of electrode (the space between two neighboring electrode lines, the height and width of electrode) on the charge–discharge characteristics were thoroughly evaluated.

2. Experimental

2.1. Fabrication of 3D-patterned and conventional flat electrodes

Cathode consisted of 80 wt% $Li_4Ti_5O_{12}$ (LTO, ISHIHARA SANGYO KAISHA, LTD.), 10 wt% acetylene black (AB, DENKI KAGAKU KOGYO KABUSHIKI KAISHA, average diameter: 35 nm) and 10 wt% poly(vinylidene difluoride) (PVdF, KISHIDA CHEMICAL Co., Ltd.) binder. Their mixture was dispersed into *N*-methylpyrrolidinone (NMP) to make the composite slurry. The weight ratio of NMP in the slurry was about 50 wt% for 3D-patterned electrodes. The slurry condition of high viscosity was selected for fabricating 3D-patterned electrodes by using the printing system described in our former report [11]. By using these materials, the 3D-patterned electrodes with 1 mA h cm^{-2} were prepared. For comparison, a conventional flat electrode was also fabricated. The composite slurry for the flat electrode consisted of LTO, AB and PVdF in the weight ratio of LTO:AB:PVdF = 8:1:1 same as that for the 3D electrode. This mixture was dispersed in NMP. The weight ratio of NMP in the slurry was controlled to be approximately 65%. The composite slurry was applied onto an aluminum current collector by using a commercial applicator (YASUDA SEIKI SEISAKUSHO, LTD.). The gap between applicator and the current collector was adjusted to control the electrode capacity per unit area for 1 mA h cm^{-2} which is as same as the 3D-patterned electrode. After the application, both types of electrodes were dried at 80 °C for 5 h under vacuum condition. Only the flat electrodes were then pressed at 30 MPa for 2 min before use. On the contrary, 3D-patterned electrodes were not pressed to maintain their structures. The shape of electrodes was observed with a laser microscope (VK-9500, Keyence).

2.2. Fabrication of cells

2032 coin-type cells were fabricated for the 3D-patterned and conventional flat electrodes by using lithium metal anode. A conventional porous polypropylene film was used as a separator. The electrolyte was 1 mol dm^{-3} $LiPF_6$ in an organic liquid mixture consisting of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (1:1 volume). Current collector was an aluminum foil. The cells were assembled in a glove box under argon atmosphere.

2.3. Evaluation of electrochemical performance

Hereafter, all the electrode potentials were referred to Li/Li^+. Cyclic voltammetry has been carried out respectively at a potential sweep rate of 20, 50 and 100 mV min^{-1} at 25 °C by using a potentiostat (HZ-3000, Hokuto Denko). Charge–discharge behaviors of the cells were recorded with a charge–discharge controller under constant current density (HJ-1001SD8, Hokuto Denko). The charge–discharge voltage region was from 1.0 V to 3.0 V and current density was 0.2 C. AC impedance measurement was performed at every 20% state of charge (SOC) at 25 °C using a potentiostat (SI1287, Solartron) and a frequency response analyzer (1252A, Solartron). The cell was discharged at the rate of 0.2 C from SOC 100% to 0%. The frequency range was 1 MHz–1 Hz, and the amplitude of voltage was 5 mV.

3. Results and discussion

3.1. Electrode structure

Fig. 1(a) shows the specifications of electrode design, in which the height (*H*) and width (*W*) of electrode line, and the space between two neighboring electrode lines are 150 μm, 70 μm and 80 μm, respectively. From the laser microscope image shown in Fig. 1(b), it was confirmed that the 3D-patterned LTO electrode fabricated using a printing apparatus had a well-defined structure according to the electrode design although the head of electrode line became slightly round. The aspect ratio (*H* value/*W* value) of this electrode pattern is about 2, but which can be increased up to over 4 (for example $W = 70$ μm and $H = 300$ μm) by using the printing apparatus manufactured by us. The size of applied area on an aluminum foil was 30 mm × 50 mm, in which no significant defect such as a shortage of the electrode line was observed.

3.2. Cyclic voltammograms

Cyclic voltammetry was carried out at 20, 50 and 100 mV s^{-1} for conventional flat and 3D-patterned electrodes, respectively.

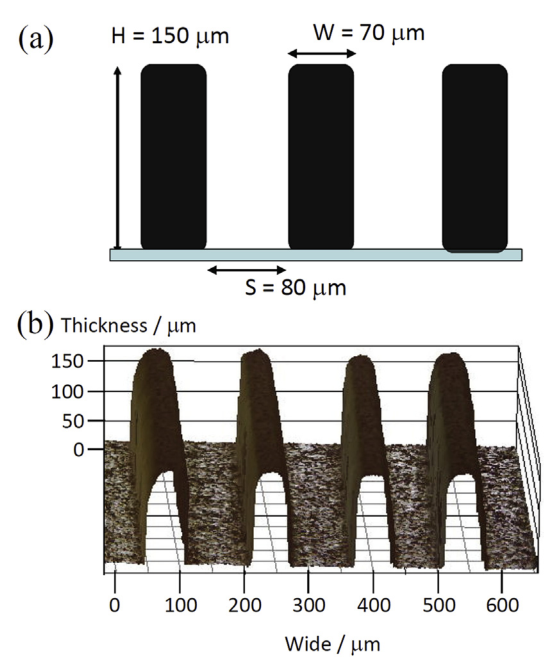

Fig. 1. The specifications of electrode design (a) and a typical laser microscope image of the prepared electrode (b).