Electrochemical performance of Sb anode using three-dimensional porous Cu foam substrate for Na-ion batteries

Do-Hwan Nam, Kyung-Sik Hong, Sung-Jin Lim and Hyuk-Sang Kwon*

Dept. of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, 335 Gwahangno, Yuseong-gu, Daejeon, 305-701, Republic of Korea

* *hskwon@kaist.ac.kr*

Introduction

Over the past few decades, Li-ion batteries (LIBs) have been widely used as power sources for mobile electronic products and power tools [1-2], and nowadays a much effort has been focused on the use of these batteries in large-scale applications such as electric vehicles, hybrid electric vehicles and electrical energy storage (EES) devices [3]. However, because the amount of the Li resources would not be sufficient to meet industrial needs in the long term, the expansion of the LiBs market takes concern on the sustainable supply of Li and the raising of the Li prices. Thus, in recent years, rechargeable sodium-ion batteries (SIBs) have received great attention as a possible alternative to replace LIBs. Owing to the abundant resource, low cost and a relatively low redox potential (0.3 V above that of Li/Li^+), NIBs are expected to be a near-term alternative for large-scale systems such as grid storages.

Despite the high specific capacity, pure sodium metal is inappropriate as an anode material for practical applications of NIBs because the dendiritc deposition of sodium during charging can cause the severe safety problems as well as the reduced capacity and increasing electrode impedance. To overcome these problems, the research for finding suitable electrode materials which have high specific capacity, low irreversible loss, high coulombic efficiency and long cycle life for SIBs have been extensively conducted. Among the various candidate materials, Sb has been considered to be very attractive anode material due to its high theoretical capacity of 660 mAh g^{-1}. However, pure Sb electrode exhibits the poor cycleability because of their significant volumetric changes (up to approximately 390%) that occurs during alloying/dealloying with Na.

In a recent communication, we reported that when the porous Cu foam [4] was used as a substrate for the Sn anode in Li-ion batteries, the Cu foam accommodated the volumetric expansion of Sn and effectively inhibited the delamination of the active materials, and hence the cyclic performance of the Sn anode was considerably improved [5]. Therefore, the objective of this work is to fabricate the Sb electrode using the highly porous Cu foam as substrate and to examine the electrochemical properties of such electrode for Na-ion batteries anode.

Experimental.

A three-dimensional porous Cu foam was prepared by the electrodeposition at a constant current density of -3 A cm^{-2} for 4 s from a Cu sulfate electrolytic bath containing 0.2 M $CuSO_4$, 0.7 M H_2SO_4, 1.2 M $(NH_4)_2SO_4$ and 0.4 mM BTA(benzotriazole) [4]. After the Cu foam was prepared, the Sb was electrodeposited on the foam substrate.

The electrochemical properties of the Sb electrode were investigated using swagelok-type cells assembled in an Ar-filled glove box. The cell is composed of a sheet of the sb electrode (with an area of 1 cm^2) and a Na metal electrode (with an area of 1 cm^2) without a separator. Electrolyte was anhydrous propylene carbonate (PC) containing 1 M $NaClO_4$. The charge/discharge characteristics of the electrode were galvanostatically examined at a current density of 0.1 C (based on mass of Sb) between 0.01 V and 1.5 V (vs. Na/Na^+). To examine the rate capabilities of the Sb/Cu foam electrode, the cell was cycled at different current densities for the following cycles in the voltage ranges between 0.01 and 2.5 V (vs. Na/Na^+) after the formation step.

Results and discussion.

As shown in Fig. 1, the Sb layer was uniformly deposited along the surface of the Cu deposits; thus, the Sb electrode exhibits a three-dimensional porous structure with a large surface area, similar to the structure of the Cu foam. Whereas the cyclic stability of the pure Sb electrode deposited on the smooth Cu sheet is poor, the Sb electrode exhibits outstanding cyclic performance; a charge capacity was maintained at 523.39 mAh g^{-1} after 100 cycles that corresponds to 84.86 % of its initial charge capacity (616.85 mAh g^{-1}). Moreover, the Sn-Co alloy electrode retains the high Coulombic efficiency of above 95 % during 100 cycles.

In addition, the Sb/Cu foam electrode exhibits an excellent performance in the rate capability as well as the cycle stability. The electrode shows the charge capacity of 605.68 mAh g^{-1} at the 0.1 C rate, but it still retains high reversible capacities of ~430 mAh g^{-1} at the 3 C rate, which is only an 30% reduction of the charge capacity. Particularly, when the current density returns to the 0.1 C after changing the current density from 0.1 to 3 C, the charge capacity was restored almost to the initial capacity with good cycle stability.

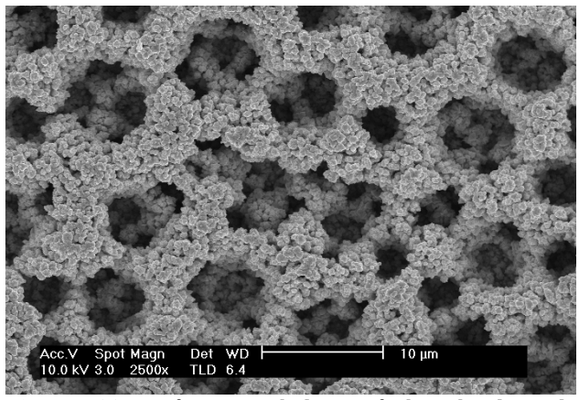

Fig. 1. (a) Surface morphology of the Sb electrode deposited onto the Cu foam substrate.

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