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A high rate and long-cycle-life anode based on micrometer-sized Pb powder for sodium-ion batteries

Changhyeon Kim[a], Huihun Kim[b], Milan K. Sadan[c], Minyeong Jeon[d], Gyu-Bong Cho[d], Tae-Hyun Nam[d], Kwon-Koo Cho[d,*,1], Jou-Hyeon Ahn[d], Hyo-Jun Ahn[d,*,2]

[a] Daejoo Electronic Materials Co., Ltd., Seohaean 148, Siheung, Gyeonggido 15094, Republic of Korea
[b] YoulChon Chemical, Doyeongwan, 112, Yeouidaebang-ro, Dongjak-gu, Seoul, Republic of Korea
[c] Research Institute for Green Energy Convergence Technology (RIGET), Gyeongsang National University, Jinju, Gyeongnam 52828, Republic of Korea
[d] Department of Materials Engineering and Convergence Technology, Gyeongsang National University, Jinju, Gyeongnam 52828, Republic of Korea

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ABSTRACT

Pb powder was investigated as an active material as anode for sodium-ion batteries. Precisely, a Pb anode comprising micrometer-sized Pb powder modified with multi-walled carbon nanotubes was fabricated. The anode showed an excellent rate capability, as well as reversible capacities of 370 mAh g^{-1} at 12.8 C (6208 mA g^{-1}). In addition, the Pb anode exhibited a stable cycle life during 1000 cycles at 10 C with a high reversible capacity of 423 mAh g^{-1}. Using electrochemical tests, scanning electron microscopy, and energy-dispersive X-ray spectroscopy, we revealed the origin of this excellent performance: the micrometer-sized Pb powder undergoes self-healing during cycling, resulting in fiber-like nanometer-sized Pb particles that reinforce the anode structure and provide fast electron transport pathways.

1. Introduction

Sodium-ion batteries (SIBs) have attracted significant interest as alternatives to lithium-ion batteries (LIBs) because of the relative abundance and low cost of Na and the comparable redox potentials of Na and Li (−2.71 and −3.05 V, respectively) [1,2]. Using techniques developed for LIBs, many researchers have developed high-performance cathode materials for SIBs, such as $NaVPO_4F$ [3], $Na_{0.44}MnO_2$ [4], $Na_xCo[Fe(CN)_6]_{0.92}{\cdot}9H_2O$ [5], polyanionic $Na_3V_2(PO_4)_2F_3$ [6], $Na_3V_2(PO_4)_3$ [7,8], layered P2-type $Na_{2/3}(Fe_{1/2}Mn_{1/2})O_2$ [9], and Prussian white ($Na_{1.92}Fe[Fe(CN)_6]$) [10]. Most cathode materials exploit the intercalation mechanism in which sodium ions are intercalated into the crystal structure. Similarly, anode materials based on intercalation, such as carbonaceous materials, have also been investigated. However, graphite, which is exclusively used in LIB anodes, cannot be used in SIBs because it cannot reversibly intercalate sodium and, thus, its sodium-storage capacity is limited [11]. Although hard carbon materials offer a reasonable capacity of approximately 250 mAh g^{-1} over 100 cycles [12], this is still lower than graphite anodes in LIBs. Therefore, to develop high-performance SIB anode materials, anode materials based on alloying mechanisms have been investigated, particularly those containing group IVA elements such as Pb, Sn, Ge, and Si. Note that these elements belong to the same group as carbon [13–16].

Although anode materials based on alloying mechanisms are relatively expensive compared to carbonaceous materials, they have remarkably high capacities. In addition, density functional theory (DFT) calculations have revealed the theoretical capacities of Pb, Sn, Ge, and Si to be 485, 847, 369, and 954 mAh g^{-1}, respectively, when they are sodiated to $Na_{15}Pb_4$, $Na_{15}Sn_4$, NaGe, and NaSi, respectively [17,18], and these values are higher than those of carbonaceous materials. Moreover, DFT calculations have also predicted operating voltages of less than 0.7 V vs. Na/Na^+. Unfortunately, the theoretical results indicate that the sodiation of Ge and Si is challenging because of their small interstitial spaces, high stiffnesses, and covalent character [18]. Therefore, of these elements, Sn and Pb remain as candidates.

* Corresponding authors at: Department of Materials Engineering and Convergence Technology, Gyeongsang National University, Jinju, Gyeongnam 52828, Republic of Korea
E-mail addresses: kkcho66@gnu.ac.kr (K.-K. Cho), ahj@gnu.ac.kr (H.-J. Ahn).
[1] ORCiD: https://orcid.org/0000-0003-0452-8788
[2] ORCiD: https://orcid.org/0000-0003-0955-124X

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