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Enhanced reversible capacity of sulfurized polyacrylonitrile cathode for room-temperature Na/S batteries by electrochemical activation☆

Huihun Kim [a], Milan K. Sadan [b], Changhyeon Kim [c], Jaejoon Jo [d], Minjun Seong [c], Kwon-Koo Cho [e,*], Ki-Won Kim [e], Jou-Hyeon Ahn [*,e], Hyo-Jun Ahn [e]

[a] YoulChon Chemical, Doyeongwan, 112, Yeouidaebang-ro, Dongjak-gu, Seoul, Korea
[b] Research Institute for Green Energy Convergence Technology (RIGET), Gyeongsang National University, Jinju, Gyeongnam 52828, Republic of Korea
[c] Daejoo Electronic Materials 148 Seohaean-ro, Siheung-si, Gyeonggi-do, 15094, Republic of Korea
[d] L&F Co. Ltd., 120, Dalseo-daero 91-gil, Dalseo-gu, Daegu 42712, Republic of Korea
[e] Department of Materials Engineering and Convergence Technology, Gyeongsang National University, 501 Jinju-daero, Jinju, Gyeongnam 52828, Republic of Korea

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ABSTRACT

Low costs and high theoretical energy densities make room-temperature Na/S batteries attractive for large-scale applications. However, obtaining sulfur cathodes with high reversible capacities remains challenging. For sulfurized polyacrylonitrile (SPAN) cathode, we found the reaction mechanism between sodium and sulfur, and then developed a method to obtain high reversible capacity by electrochemical activation. During the first discharge (sodiation), one sodium per sulfur atom reacts irreversibly with the conjugated carbon backbone, which reduces the resistance of SPAN. Upon further sodiation, sodium reversibly reacts with free sulfur generated by cleaving C–S and S–S bonds in SPAN to form Na_2S. After simple activation, i.e. further sodiation, 1.8 sodium atoms per sulfur atom, the reversible discharge capacity reaches 1502 mAh $g^{-1}_{\text{-sulfur}}$, similar to the theoretical capacity of Na_2S, which is the highest value ever reported. After 100 cycles, the capacity remains at 1405 mAh $g^{-1}_{\text{-sulfur}}$; thus, the energy density of SPAN is 543 Wh kg^{-1}, much higher than the theoretical value for lithium-ion batteries. The reported reaction mechanism and activation process provide new strategies for room-temperature Na/S batteries.

1. Introduction

The development of large-scale batteries has become urgent because of the demand for electric vehicles and energy storage systems. Lithium-ion batteries (LIBs) have been the most popular energy storage systems for both portable and large-scale applications owing to their high energy densities and long cycle lives [1]. However, the high cost and limited availability of LIB electrode materials, such as Li, Co, and Ni, remain serious concerns [2]. Among various large-scale batteries, sodium/sulfur (Na/S) batteries have been commercialized because of their low costs and high theoretical energy densities [3]. In particular, the electrode raw materials, i.e. Na and S, are abundant and cheap (Na: 28400 mg kg^{-1} in the Earth's crust and 11000 mg L^{-1} in seawater; S: 340 mg kg^{-1} in the Earth's crust) [4]. The commercial Na/S batteries operate at a high temperature (300 °C) with molten sulfur and sodium electrodes [5]; however, these corrosive molten electrodes lead to serious safety problems and high maintenance costs. To overcome these issues, our group reported a solid-state Na/S battery that can operate at room temperature (RT Na/S battery) for the first time in 2006 [6]. In addition, since one S atom can react with two Na atoms to form Na_2S (Eq. (1)), the RT Na/S battery exhibits a higher theoretical energy density of 1274 Wh kg^{-1} than a commercial Na/S battery or Li-ion battery.

$$S + 2Na \leftrightarrow Na_2S \quad (1)$$

However, RT Na/S batteries still face many severe challenges, such as poor cycle lives and reversible capacities lower than the theoretical values, which could be related to the poor electrical conductivity of elemental sulfur and the dissolution of sodium polysulfides in ether-

☆ sulfurized polyacrylonitrile, SPAN; lithium-ion batteries, LIBs; polyacrylonitrile, PAN; X-ray diffraction, XRD; scanning electron microscopy, SEM; energy-dispersive X-ray spectroscopy, EDS; X-ray photoelectron spectroscopy, XPS; Fourier-transform infrared, FTIR; diethyl carbonate, DEC; galvanostatic intermittent titration technique, GITT; Cyclic voltammetry CV

* Corresponding authors.
E-mail addresses: kkcho66@gnu.ac.kr (K.-K. Cho), ahj@gnu.ac.kr (H.-J. Ahn).

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