Journal of Alloys and Compounds 868 (2021) 158850

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Influence of cycling stability on structure and properties of $MnCo_2S_4$ nanocomposite for high-performance supercapacitors

Damin Lee [a,b], Hyun Woo Lee [c], Sanjay Mathur [b,*], Kwang Ho Kim [a,c,**]

[a] Global Frontier R&D Center for Hybrid Interface Materials, Pusan National University, San 30 Jangjeon-dong, Geumjeong-gu, Busan 609-735, Republic of Korea
[b] Institute of Inorganic Chemistry, University of Cologne, Greinstr. 6, Cologne, Germany
[c] School of Materials Science and Engineering, Pusan National University, San 30 Jangjeon-dong, Geumjeong-gu, Busan 609-735, Republic of Korea

ARTICLE INFO

Article history:
Received 1 November 2020
Received in revised form 15 January 2021
Accepted 19 January 2021
Available online 2 February 2021

Keywords:
Hydrothermal method
Nanostructure
Manganese-cobalt
Metal sulfides composite
Supercapacitors

ABSTRACT

Mesoporous $MnCo_2S_4$ composites directly grown on porous Ni foam were prepared by a facile hydrothermal method for high-performance supercapacitors. The nanostructure of $MnCo_2S_4$ composite electrodes plays an important role in achieving desirable electrical properties by providing a large surface area that greatly improves the electrode/electrolyte contact area and shortens the ion diffusion paths. As a result, the $MnCo_2S_4$ electrode exhibits the advantages of high conductivity and a fast-redox reaction rate. Moreover, metal sulfides are receiving more attention for use in supercapacitors owing to their higher electrical conductivity than those of metal oxides/hydroxides. However, these sulfides are difficult to apply in practice owing to a low potential window. In this study, to compensate for these shortcomings, we experimented with adding glycerol and ethylene glycol to the $MnCo_2S_4$ composite. Among the obtained composites, the glycerol-$MnCo_2S_4$ electrodes showed high-capacity retention after many cycles and a remarkable maximum specific capacitance of 1218.7 F g^{-1} at 3 A g^{-1}, which was significantly higher than that of other electrodes. The cycling stability of the glycerol-$MnCo_2S_4$ composite electrode was also measured to be the highest at 92.4% after 5000 cycles. In addition, the glycerol-$MnCo_2S_4$ composite was confirmed to have the highest specific capacitance, after 5000 cycles (484.2 F g^{-1} at 3 A g^{-1}). In addition, we fabricated an asymmetric supercapacitor employing the glycerol-$MnCo_2S_4$ composite as the positive electrode and graphene as the negative electrode, which exhibited a high energy density of 32.9 W h kg^{-1} at a power density of 295.2 W kg^{-1} and a remarkable cycling stability, with 87.7% capacitance retention after 5000 cycles. These advantages show that the glycerol-$MnCo_2S_4$ electrodes prepared by the hydrothermal method could be a promising positive electrode material for high-performance asymmetric supercapacitors.

1. Introduction

Supercapacitors (SCs) have attracted attention recently owing to their fast charge and discharge rates, high power density, long cycle life, and higher reliability than that of lithium ion batteries. Generally, the performance of SCs is influenced by the electrode materials, electrolytes, and assembled devices; however, the electrode material is the most important factor contributing to the overall device performance [1,2]. Based on the charge storage mechanism, SCs are classified as either electric double layer capacitors (EDLCs) or faradaic capacitors. Unlike EDLCs, which use a carbon active material as an electrode, faradaic capacitors employ a binary metal composite structure with various types of metal oxides or hydroxides as the electrode. Among these materials, transition metal-based composites are extensively used as precursors to prepare electrodes for SCs [3]. Transition metals have many electrons with similar energies, which stabilizes the various oxidation states and facilitates the redox reaction [4,5]. Faradaic capacitors that charge and discharge through redox reactions experience a positive effect when transition metals are used, because of which redox reactions occur more easily on the electrode surface. NiO [6], RuO_2 [7], CuO [8], MnO_2 [9], Co_3O_4 [10], $Ni(OH)_2$ [11], and their associated compounds have been used as electrode materials in faradaic capacitors. Yan et al. reported a $Ni(OH)_2$/graphene composite with a specific capacitance of 218.4 F g^{-1} [12]. Jin-Hui et al. showed that the

* Corresponding author.
** Corresponding author at: School of Materials Science and Engineering, Pusan National University, San 30 Jangjeon-dong, Geumjeong-gu, Busan 609-735, Republic of Korea.
E-mail addresses: sanjay.mathur@uni-koeln.de (S. Mathur), kwhokim@pusan.ac.kr (K.H. Kim).

https://doi.org/10.1016/j.jallcom.2021.158850
0925-8388/