Electrochimica Acta 69 (2012) 358–363

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

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

Performance enhancement of Li-ion batteries by the addition of metal oxides (CuO, Co_3O_4)/solvothermally reduced graphene oxide composites

Kwang-Hyun Kim[a], Dong-Won Jung[a], Viet Hung Pham[a], Jin Suk Chung[a], Byung-Seon Kong[b], Jung Kyoo Lee[c], Ketack Kim[d], Eun-Suok Oh[a,*]

[a] School of Chemical Engineering & Bioengineering, University of Ulsan, Daehak-ro 102, Nam-gu, Ulsan 680-749, Republic of Korea
[b] KCC Central Research Institute, 83 Mabook-Dong, Giheung-Gu, Yongin, Kyunggi-Do 446-912, Republic of Korea
[c] Department of Chemical Engineering, Dong-A University, 840 Hadan 2-dong, Sahaku, Busan 604-714, Republic of Korea
[d] Department of Chemistry, SangMyung University, 7 Hongji-dong, Jongno-gu, Seoul 110-743, Republic of Korea

ARTICLE INFO

Article history:
Received 16 November 2011
Received in revised form 2 March 2012
Accepted 3 March 2012
Available online 9 March 2012

Keywords:
Lithium ion batteries
Anode active materials
Solvothermally reduced graphene oxide
Cobalt oxide
Copper oxide

ABSTRACT

Solvothermally reduced graphene oxide (STRG) that was synthesized using N-methyl-2-pyrrolidone (NMP) solvent was first employed as an conducting additive up to 15 wt% to commercial graphite anodic material. Due to numerous functional groups on the surface of the STRG, the reversible capacity decreased as the amount of STRG in the anode increased. To overcome this disadvantage, nanosized metal oxides such as CuO and Co_3O_4 were supported on the STRG and a small amount of the composites was added to commercial graphite in order to enhance cyclic performance of the anode. A variety of characterization techniques showed that the composite additive significantly increased the reversible cyclic capacity by reducing the irreversible capacity of STRG and by providing more space for lithium ion intercalation.

1. Introduction

Graphite has been used as an anode material for LIBs [1–4]. However, its capacity is insufficient for use in future applications such as electronic vehicles and high-performance mobile electronics. Therefore, much attention has been paid to the development of high capacity anode materials; silicon and tin have been some of the most studied materials for this purpose. Recently, a few studies were recently reported that the use of transition metal oxides (MOs) as anode materials significantly enhanced reversible LIB capacity [5–10]. For example, CuO (670 mAh g^{-1}) and Co_3O_4 (890 mAh g^{-1}) showed much greater theoretical capacity than commercial graphite [7,8]. However, these MOs undergo large volume changes during lithium insertion/extraction processes [11–16], CuO (174%) [15] and Co_3O_4 (100%) [16], develop significant mechanical stresses in the electrode, and cause rapid capacity fading. A variety of methods have been introduced to resolve these problems, including modified synthesis methods for nanosized MOs [11,17–20].

Alternatively, graphene nanosheets were very recently studied to assess their possible use as anode materials [21–23]. Due to lithium ion storage on each side of the graphene sheets, on active sites, and in the nanocavity, the graphene nanosheets increase the reversible capacity of LIB anodes [21,22]. However, Yao et al. reported that the use of graphene alone as an active material decreased LIB capacity compared to a graphite electrode, while graphene as a flexible buffer to high capacity tin oxide significantly enhanced LIB performance [23]. Guo et al. [24] reported that when graphene was added to artificial graphite as a conductive material, the LIB cell showed higher reversible capacity and better cycling stability. It has been also reported that MO/graphene composites increased the reversible capacities compared to carbonaceous materials due to the formation of the conductive graphene network with nanosized MO particles and the elastic buffer by graphene [20,25–27]. As a summary from previous works, graphene could be a good buffer to significant volume change regardless of its ability to increase the reversible capacity.

In this study we have thoroughly investigated the effect of a solvothermally reduced graphene oxide (STRG) as an additive in the LIB anode. The STRG sample was synthesized via solvothermal reduction, which is a simple and effective method for producing chemically converted graphene [28], using NMP solvent as a reducing agent. Also, its electrochemical performance as an anode

---

* Corresponding author. Tel.: +82 52 259 1689; fax: +82 52 259 2783.
E-mail address: esoh1@ulsan.ac.kr (E.-S. Oh).

0013-4686/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2012.03.005

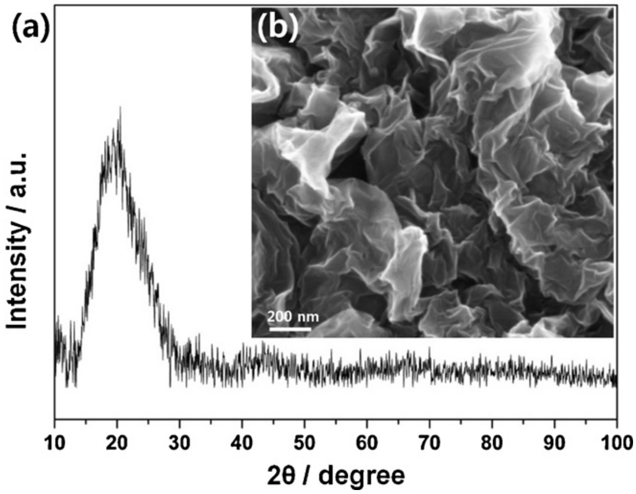

Fig. 1. (a) X-ray diffraction pattern and (b) FE-SEM image of STRG.

material was investigated through a variety of characterization techniques. Moreover, its buffering effect on high-capacity CuO and Co_3O_4 nanoparticles was also tested and characterized by the addition of 1 wt% of the composites to commercial graphite.

2. Experimental

Chemically functionalized graphene nanosheets were prepared by the solvothermal reduction of graphene oxide as described in detail in our previous paper [28]. The graphene oxide was reduced in a mixture of water and NMP at 180 °C for 5 h. The STRG sample was added to ethylene glycol (EG) and this solution was heated to 110 °C with the drop-wise addition of 1 M NaOH to adjust the pH to 10. Either $CuCl_2{\cdot}2H_2O$ or $CoCl_2{\cdot}6H_2O$ (Sigma–Aldrich Inc.) as a precursor was dissolved in EG, mixed with the STRG solution and stirred for 3 h to synthesize Cu or Co oxide particles that were supported on the STRG. Then, this solution was washed in de-ionized water and ethanol, dried in a vacuum oven at 60 °C for 4 h, and finally annealed in air at 350 °C for 2 h.

The crystal structures and morphologies of the composites were characterized using XRD (Rigaku, RAD-3C), FE-SEM (Carl Zeiss, Supra 40) and TEM (Jeol, Jem-2010). From the XRD results, the oxides were CuO and Co_3O_4 in the composites, respectively. For convenience, Cu oxide-STRG and Co oxide-STRG composites will hereafter be referred to as CuO-STRG and Co_3O_4-STRG, respectively. The Raman spectra (Renishaw Raman spectrometer) were also measured using a laser of 632.8 nm to observe the structural changes of STRG during the composite synthesis. The weight percentages of CuO and Co_3O_4 in the composites were measured using an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Thermo Electron, iCAP6500). The electrochemical characterization was performed through CR2016-type coin half-cells with the working electrode containing STRG, Co_3O_4-STRG, or CuO-STRG and lithium metal as a counter electrode. The STRG-containing electrodes consisted of physically mixed STRG/C (graphite, Sodiff Co., Korea) 80 wt% composites, 5 wt% vapor growth carbon fiber, and 15 wt% polyvinylidene fluoride (Solef 50130, Solvey Co.). The compositions of STRG/C were 0/80, 1/79, 5/75, 10/70, and 15/65, respectively. The CuO-STRG/C or Co_3O_4-STRG/C

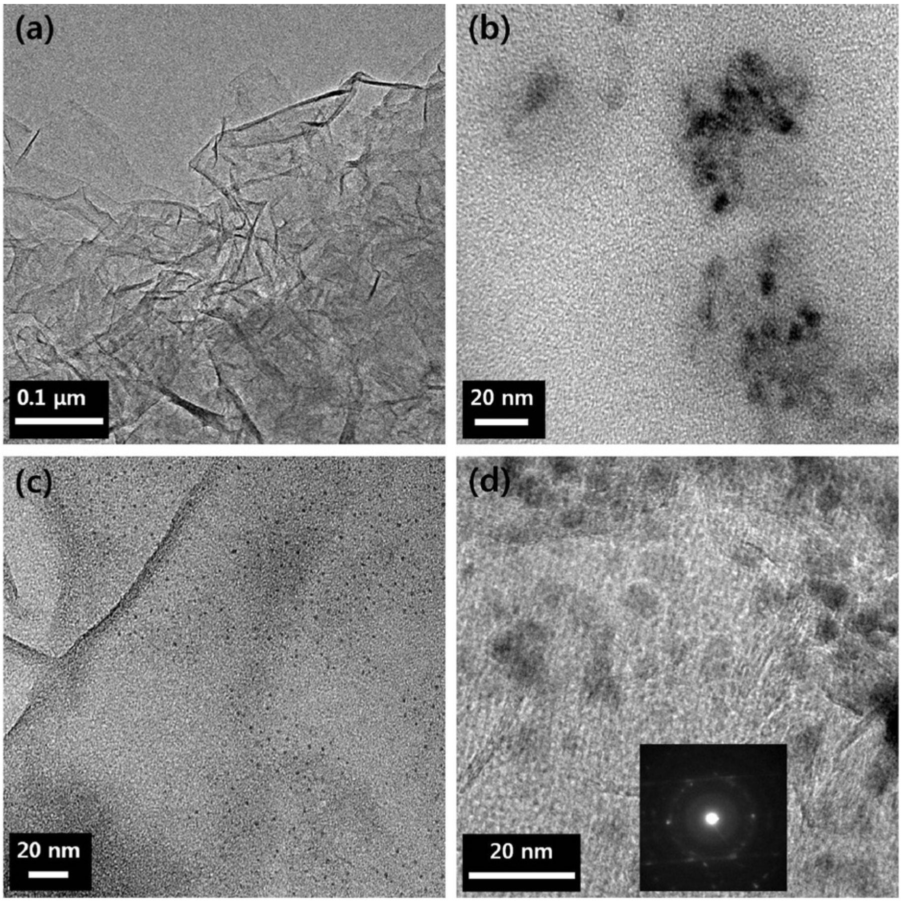

Fig. 2. (a) HR-TEM image of STRG, TEM images of (b) Co_3O_4-STRG and (c) CuO-STRG, and (d) HR-TEM image of CuO-STRG. The inset in (d) is the electron diffraction pattern of the CuO particles.