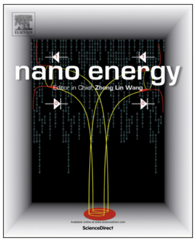
Nano Energy (2014) 4, 97–104

Available online at www.sciencedirect.com

ScienceDirect

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



RAPID COMMUNICATION

Novel transition-metal-free cathode for high energy and power sodium rechargeable batteries

Haegyeom Kim[a], **Young-Uk Park**[a], **Kyu-Young Park**[a], **Hee-Dae Lim**[a], **Jihyun Hong**[a], **Kisuk Kang**[a,b,*]

[a]*Department of Materials Science and Engineering, Research Institute of Advanced Materials (RIAM), Seoul National University, 599 Gwanak-ro, Gwanak-gu, Seoul 151-742, Republic of Korea*
[b]*Center for Nanoparticle Research, Institute for Basic Science (IBS), Seoul National University, Seoul 151-742, Republic of Korea*

Received 23 September 2013; received in revised form 4 December 2013; accepted 21 December 2013
Available online 1 January 2014

KEYWORDS
Sodium;
Batteries;
Electrochemistry;
Energy storage;
Graphite

Abstract
A low-cost and high-performance energy storage device is a key component for sustainable energy utilization. Recently, sodium (Na) ion batteries have been highlighted as a possible competitor to lithium (Li) ion batteries due to their potential merit in the cost effectiveness. Na resources are earth-abundant, and Na electrochemistry shares many similarities with Li. However, their relatively low energy/power densities and unreliable cycle stability need to be addressed. Herein, we propose a novel high-performance cathode for Na rechargeable batteries based on mass-scalable functionalized graphite nanoplatelets. This new class cathode material can deliver a high energy of $\sim 500\ \mathrm{W\,h\,kg^{-1}}$ without noticeable capacity decay after 300 cycles. Furthermore, it can retain an energy of $\sim 100\ \mathrm{W\,h\,kg^{-1}}$ at a power of $\sim 55\ \mathrm{kW\,kg^{-1}}$ (less than 10-s charge/discharge), which is the highest among cathodes for Na ion batteries. This transition-metal-free high-performance cathode is expected to lead to the development of low-cost and high-performance Na rechargeable batteries.

Introduction

Developing a reliable energy storage system (ESS) is one of the most important issues in moving toward a sustainable society [1-3]. Because electricity production from renewable energy (*i.e.* solar, wind and geothermal energy) does not coincide with consumption time, the ESS is required to account for the discrepancy. Lithium ion batteries (LIBs)

---

[*] Corresponding author at: Department of Materials Science and Engineering, Research Institute of Advanced Materials (RIAM), Center for Nanoparticle Research, Institute for Basic Science (IBS), Seoul National University, 599 Gwanak-ro, Gwanak-gu, Seoul 151-742, Republic of Korea. Tel.: +82 2 880 7088; fax.: +82 2 885 9671.
E-mail address: matlgen1@snu.ac.kr (K. Kang).

2211-2855/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.nanoen.2013.12.009

have been considered as the leading candidates for large-scale ESS due to their relatively high energy, power density and stable cyclability [4-9]. However, the high cost of LIBs (partly due to the use of costly transition metals such as Co and Ni), and the arguable shortage of Li resources has limited their applications to date [10-14].

In the respect of materials cost, exploring energy storage chemistry based solely on earth-abundant elements is quite advantageous. Na ion batteries (NIBs), in particular, have been extensively studied as an alternative to LIBs in recent years due to earth-abundant Na and its similar electrochemical properties with Li. It was reported that NIB can approach electrochemical performance comparable to LIB [15-17]. However, NIB at present also uses cathodes based on transition metal redox elements, which are typically much more expensive than Li or Na itself. This significantly dilutes the cost merit of NIB. Furthermore, during the battery operation, the larger ionic size of Na than Li induces more severe lattice expansion and contraction during (de) insertion in typical intercalation compounds, which often leads to faster cycle deterioration and inferior power capability [13,18-20].

In resolving these issues, here, we propose a novel NIB cathode based on a transition-metal-free carbonaceous material with a non-intercalation-based Na storage mechanism. Starting from natural graphite, functionalized graphite nanoplatelets were fabricated *via* simple scalable routes, which could control the chemical composition and porous nanostructure of the sample in one-step. By using surface reactions between Na and functionals on graphite nanoplatelets, (i) no significant lattice change occurred during battery cycling, and (ii) much faster Na kinetics could be achieved through porous network without solid-state diffusion [21,22]. Furthermore, the high electrical conductivity of the material could aid in improving the rate capability [23,24]. While previous studies of graphite-based electrodes are mostly found in anode applications for NIB and only very recently its cathode application was discovered, [25-27] this work manipulated the carbon into a cathode with a tunability of composition and nanostructure by simple one-step chemical modification. The functionalized graphite cathode could deliver the energy of $\sim$500 W h kg^{-1} without capacity decay during 300 battery cycles and could also exhibit an unprecedentedly high power of $\sim$55 kW kg^{-1} with a less-than-10 s charge/discharge rate for NIB. The energy and power density of the porous functionalized graphite cathode exceeded the performance of recently reported NIB cathode materials [15-17,23,24,28-30].

Experimental section

Fabrication of functionalized graphite nanoplatelets

Graphite oxide (GO) was first fabricated by modifying the Hummers method [31]. Graphite (5 g) was dispersed in a solution of $NaNO_3$ (5 g) and H_2SO_4 (225 mL), which was stirred for 30 min in an ice bath. $KMnO_4$ (30 g) was added to the resulting solution, followed by stirring at 50 °C for 2 h. Deionized (DI) water (500 mL) and H_2O_2 (30 mL, 35%) were slowly added to the solution. The solution was filtered and washed with HCl (750 mL, 10%). Additional washing/filtering was performed using concentrated HCl (500 mL, 37%) to retrieve the GO powder. The samples were annealed at 120 °C for 6 h to generate the functionalized graphite nanoplatelets.

Characterization

The structure of the functionalized graphite nanoplatelet was analyzed with an X-ray diffractometer (XRD, D2PHASER) using Cu Kα radiation. X-ray photoelectron spectroscopy (XPS, AXIS-HSi) was used to quantify the functionals in the samples. Morphology was examined using field-emission scanning electron microscopy (FE-SEM, SUPRA 55VP) and high-resolution transmission electron microscopy (HR-TEM, JEM-3000F). A focused ion beam (FIB, AURIGA) was used at 30 kV and 600 pA after Pt coating. The carbon structure was analyzed using a high-resolution dispersive Raman microscope (LabRAM HR UV/Vis/NIR). The surface area and pore volume were determined using the Brunauer-Emmett-Teller (BET) method. Electrochemical impedance spectroscopy (EIS) data were recorded from 1 MHz to 100 mHz using a potentiostat/galvanostat (VSP-300, Bio-Logic, France).

Electrochemical characterization

Electrodes were prepared by mixing the active material (70 wt%) with polyvinylidene fluoride binder (20 wt%) and super-P (10 wt%) in an *N*-methyl-2-pyrrolidone solvent. The resulting slurry was uniformly pasted onto Al foil, dried at 120 °C for 2 h, and then roll-pressed. A total of 1-2 mg cm^{-2} of the active material was loaded onto the electrode. Test cells were assembled into a two-electrode configuration with a Na metal counter electrode (Sigma-Aldrich), a glass microfiber filter separator (grade GF/F; Whatman, USA), and an electrolyte of 1 M $NaBF_4$ or $NaClO_4$ in propylene carbonate (PC, Sigma-Aldrich) in a glove box. Cyclic voltammetry and electrochemical profiles were obtained over a voltage range of 4.3-1.0 V using a multichannel potentiogalvanostat (WBCS 3000, WonATech).

Results and discussion

Functionalized graphite nanoplatelets were synthesized by the controlled reduction of graphite oxides (GO) with a low-temperature annealing in the presence of residual HCl as we recently reported [21]. After chemical oxidation, the XRD peak of pristine graphite (002) shifted to a lower angle, indicative of expansion of graphene interlayers as a result of a large amounts of C-O or C=O formation in the graphite (Figure 1a) [32]. However, the characteristic XRD peak of GO disappeared after the annealing process at 120 °C, shown as the upper blue pattern in Figure 1a. This implied that C-O or C=O functional groups were removed and the long-range ordering along the perpendicular direction of basal graphene planes was lost at this temperature [33]. XPS analysis in Figure 1b and c indicated the partial reduction of GO in which the amount of functional groups of C-O (286.6 eV) and C=O (287.6 eV) were significantly reduced [34]. Raman spectroscopy in Figure S1 also confirmed the GO was partially reduced with some remaining functional groups in the sample [35].