

RAPID COMMUNICATION

Surface capacitive contributions: Towards high rate anode materials for sodium ion batteries



Sheng Li, Jingxia Qiu, Chao Lai, Min Ling, Huijun Zhao, Shanqing Zhang*

Centre for Clean Environment and Energy, Environmental Futures Research Institute, Griffith School of Environment, Griffith University, Gold Coast QLD 4222, Australia

Received 14 November 2014; received in revised form 16 December 2014; accepted 22 December 2014
Available online 31 December 2014

KEYWORDS

Sodium ion battery;
Capacitive;
Anode;
Graphene;
Intercalation

Abstract

Due to the poor transportability of sodium ions, conventional sodium ion batteries (SIBs) cannot deliver sufficient capacity for high rate applications. Surface-induced capacitive processes (SCP) (e.g. capacitance and pseudocapacitance) could provide fast charge/discharge capacity in conjunction with the capacity provided by diffusion-controlled intercalation processes (DIP) to address this issue. For the first time, SCP was used to design a hierarchical layered graphene composite as an anode material for high rate SIBs. The contributions of the individual sodium storage processes were quantitatively evaluated, verifying the proposed mechanism. The resultant SCP-enhanced SIB delivers an outstanding rate capacity of 120 mAh/g at 10 A/g, which is among best of the state-of-the-art carbon-based SIBs. It also demonstrates exceptional cycling stability, retaining 83.5% capacity of 142 mAh/g at 0.5 A/g after 2500 cycles.

© 2015 Published by Elsevier Ltd.

Introduction

High rate charge/discharge energy storage technology is important for renewable energy devices. Although lithium ion batteries (LIBs) have had unprecedented achievements in both the theoretical and practical fields in recent decades [1–4], more

economical, sustainable and scalable energy storage devices are needed to tackle the problems of high cost and limited lithium sources. Sharing similar chemistry with LIBs, sodium ion batteries (SIBs) are considered one of the most promising alternatives due to their low cost and enormous abundance of sodium [5–8]. Most electrode materials for LIBs however, cannot be easily adopted for SIBs because Na ions are 55% larger in radius than Li ions. In particular, the intercalation of Na ions is rarely achieved using common graphite anodes, the most widely commercialized anode material for LIBs [9–11].

*Corresponding author.

E-mail address: s.zhang@griffith.edu.au (S. Zhang).

Various materials such as alloys [12,13], metal sulphates [14] and metal oxides [15–20] have been vigorously investigated for SIB anodes. Carbonaceous materials are considered the best option because they have high electronic conductivity, low cost, are renewable and environmentally friendly [21]. To date there are two mechanisms of Na ion storage in carbon materials: (a) the intercalation of Na ions into the expanded graphite layered structure, where the interlayer spacing (d) is greater than 0.37 nm [22]. This is termed a diffusion-controlled intercalation process (DIP) [23]. It is commonly assumed that high rate capacity cannot be achieved by DIP for SIBs due to the large size of Na ions and their poor mass transportability into the crystals. (b) The energy storage mechanism of the surface-induced capacitive process (SCP) includes not only double layer capacitance but also the adsorption of Na ions onto the surface defects and nanovoids [8]. Furthermore, surface functional groups can also contribute SCP performance at a working voltage as cathodes [24–26]. In general, SCP is considered an adjunctive property for batteries and main stream research is still focusing on DIP [7,23,27,28]. Hybrid supercapacitor systems depending on several electrodes or one electrode with several components have been explored for LIBs [29,30]. Following this line of thinking, utilizing SCP in electrode materials for SIBs could boost the rate capability due to fast capacitive reactions.

Since graphene is highly conductive with an extremely large surface area [31,32], it is an ideal primary material for constructing an expanded layered composite with a secondary hierarchical structure to utilize both DIP and SCP contributions. Inspired by the wet-carbonization process for producing amorphous carbon (AC) [33–35], we use graphene oxides (GO) and glucose solutions as precursors to synthesize an amorphous carbon/graphene (AC/G) composite for evaluating the SCP contributions to SIBs.

Under hydrothermal reaction conditions, polymerizations between the hydroxyl functional groups of glucose and the oxygen-containing functional groups (carbonyl, carboxylic, bridge oxygen and hydroxyl groups) of GO occur. Glucose molecules can be initially directed onto the surface of graphene sheets, then subject to a wet carbonization process, leading to AC/G composites. As shown in Figure 1, the composite is composed of graphene layers with the as-formed AC spheres acting as pillars between the layers (~ 100 nm). The nanopillars prevent the graphene sheets from restacking and maintain the multi-layered carbon structure, leading to a large surface area. Abundant defects can be created in the composite during the reaction and a subsequent annealing process. This structure benefits the SCP. The reaction process also creates many distortional graphite nanocrystallites (DGNs) by twisted layer-stacking graphene, with “expanded” interlayer space (~ 0.4 nm) to facilitate the DIP of Na ions. DGNs could also secure the structural stability during SCP and DIP. It was expected that the resultant composite could meet the requirements for both SCP and DIP, and be a simple, low cost and high performance rate anode material for SIBs.

Results and discussion

The multi-layered structure can be easily observed from scanning electron microscope (SEM, Figure 2a and b). The distances between the layers vary from approximately 50 nm

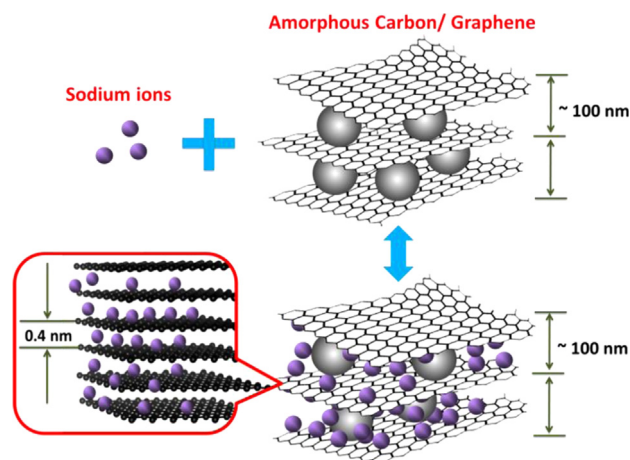


Figure 1 Schematic diagram of Na ions storage mechanisms of AC/G nanocomposites.

to 200 nm and are substantially larger than the size of Na ions. The multi-layered morphology delivers a high BET surface area of 601.7 m²/g (Figure S2). These properties facilitate rapid mass transport and insertion of Na ions. Pore size distribution measurement (inset, Figure S2) shows the presence of both micropore structures (<1 nm) and macro-pore structures (>50 nm).

From transmission electron microscopy (TEM, Figure 2c), twisted wrinkles on the surface of the graphene sheets could be observed, creating DGNs with large interlayer d . The fact that the AC spheres have a diameter of *c.a.* 150 nm is in line with the distance observed in the SEM results. The DGNs layers are readily found as seen in Figure 2d. These long-range disordered structures not only provide more entrances for DIP of Na ions, but also offer plentiful surface defects, assisting the adsorption kinetics of the SCP. The magnified TEM image of the DGN in Figure 2e demonstrates a 0.4 nm interlayer distance (Figure 2f). The calculation of cycle radius from selected area electron diffraction (SAED) patterns (Figure 2g) provides the same d value as the TEM analysis.

Raman spectroscopy analysis was conducted to evaluate the extent of disorder of the sp^2 structure in the GO and AC/G samples in Figure S3. Two obvious carbon D band and G band peaks could be observed for both samples. It has been established that the relative integral intensity ratio (i.e., peak area ratio) of the D to G bands (I_D/I_G) can be considered as an indicator of the disorder of carbon [27]. The raw graphite usually has a very weak D band because of its limited defects structure [36]. Both GO and AC/G present high I_D/I_G values (1.39 for GO and 1.54 for AC/G), suggesting high disorder of their sp^2 structure. The type of the disorders and the surface conditions could be further characterized by X-ray Photoelectron Spectroscopy (XPS) analysis. From C 1s patterns (Figure S4c and S4d), peaks of oxygen functional groups can be divided from C 1s spectra of GO. These peaks decreased dramatically after the hydrothermal treatment, which suggests that these functional oxygen groups have been reacted under the hydrothermal reaction conditions, i.e., the reduction of GO occurs. Though there are very small amount of oxygen functional groups in AC/G sample, these functional groups are not reactive in anode potential range [24–26]. The mechanism of AC/G for SCP sodium storage is based

Download English Version:

<https://daneshyari.com/en/article/1557241>

Download Persian Version:

<https://daneshyari.com/article/1557241>

[Daneshyari.com](https://daneshyari.com)