Res Chem Intermed (2014) 40:2501–2507
DOI 10.1007/s11164-014-1660-3

Preparation and characterization of anode materials using expanded graphite/pitch composite for high-power Li-ion secondary batteries

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Received: 20 October 2012 / Accepted: 20 January 2013 / Published online: 21 May 2014

Abstract Expanded graphite was prepared by the intercalation of natural graphite using ammonium peroxodisulfate as an oxidizing agent and a high purity of sulfuric acid as an intercalate. The amounts of oxidizing agent and intercalate were changed to determine the preparation conditions of expanded graphite as the anode material for high-power Li-ion batteries. The expanded graphite was tested as the anode material and further composited with the different amounts of petroleum pitch to improve the electrochemical properties. Although the expanded graphite anode showed the improved electrochemical properties such as initial reversible capacities of around 400 mAh/g and a charge capacity at 5 C-rate of 83 mAh/g as compared with those for the natural graphite anode of 378 and 19.4 mAh/g, respectively, it still had some weak points for a high-power anode material such as low initial efficiency and potential plateaus with the stage characteristic. The anode composites with high performance could be obtained by compositing the expanded graphite and the petroleum pitch at the ratio of 1:2, showing an improved initial efficiency of 78 % and decreased potential plateaus with 389 mAh/g of the initial reversible capacity.

Keywords Expanded graphite · Petroleum pitch · Anode materials · Lithium-ion secondary battery

Introduction

The advantages of secondary lithium-ion batteries (LIB) are their high operating voltage, high specific energy, very slow self-discharge, and no memory effect [1]. A LIB consists of two electrodes between which a porous insulating separator prevents short-circuiting, an electrolyte conducting lithium-ions from the negative

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electrode to the positive electrode during discharge, and a reversed flow during charge [2].

Carbon materials are the most actively used as anode materials for LIB due to their small surface change, stable structure, and favorable price [3, 4]. In order to apply LIB for electric vehicles and hybrid electric vehicles, they require not only high energy density but also high-power density. Recently, natural graphite has been considered as a promising anode material for lithium-ion batteries due to its high reversible capacity, appropriate charge/discharge profile, and low cost. However, low first cycle efficiency and poor cycle stability has limited its practical use [5–7].

Expanded graphite (EG) can be produced by exfoliation of graphite intercalation compounds with Brönsted acids or expandable graphite [8, 9]. Natural graphite is first converted to intercalated or expandable graphite through chemical oxidation in the presence of concentrated H_2SO_4. EG is then obtained by rapid expansion and exfoliation of expandable graphite in a furnace above 600 °C. When the EG having a wider layer distance is applied to the anode materials for LIB, it is assumed that the intercalation/deintercalation of Li-ion can be done with ease as compared with the case of graphite [10]. Since the petroleum pitch is non-crystalline carbon, it has a disordered structure and its adjacent carbon layers are arranged irregularly. So, petroleum pitch can display a higher reversible capacity than graphite due to having a complex crystalline structure [11]. Anode materials with high rate capability for LIB have been investigated by using the mixture of various carbon materials such as graphite and petroleum pitch [12–15].

The object of this study is to determine the preparation conditions of EG as the anode materials for high-power LIB. The obtained EG would be further composited by mixing with the petroleum pitch and the heat treatment in order to make the spherical shape of carbonaceous composites, expecting an improved performance as the anode material.

Materials and methods

The flake type of natural graphite with well-developed lamella structure (thickness: $10 \sim 15$ μm) was used to make the EGs, and the EGs were prepared by using ammonium peroxodisulfate ($(NH_4)_2S_2O_8$, assay 98.0 %; Junsei Chem) as the oxidizing agent and high purity of sulfuric acid (H_2SO_4, assay 96.6 %; J.T. Baker) as the intercalate. The obtained EG samples were named as SnAmTz, where Sn is the amount of sulfuric acid (g/20 g of graphite), Am the amount of ammonium peroxodisulfate (wt%), and Tz the heat treatment temperature (°C). The EG was tested as the anode materials after the heat treatment at 1,000 °C and pulverizing the heat-treated EGs below 30 μm with a planetary mill. The EG was further composited with the petroleum pitch (softening point 250 °C) at different mass ratios of 1:1, 1:2, and 1:4, called P/EG(1:1), P/EG (1:2), and P/EG(1:4). The microstructure of the EGs was observed by scanning electron microscope (SEM, 3500N; Hitachi Science System, Japan), and the crystallinity of EGs was analyzed by X-ray diffraction (XRD; CuKa = 1.54 Å; X'pert-Pro, PANalytical) and Raman spectrums (LabRam HR, Ar-ion laser; Jobin–Yvon).

The electrodes were prepared by mixing 93 wt% of the anode active materials and 7 wt% of polyvinylidene fluoride (PVDF) binder dissolved in 1-methyl-2-pyrrolidinone (NMP) with a homogenizer at rotation speeds of 4,000 ~ 5,000 rpm to form slurry. The mixed slurry was then coated on the copper foil by the Doctor Blade method and dried at 100 °C in a vacuum oven for 24 h before being compressed by a roll press at 80 °C. The prepared anodes of 2.5 × 2.5 cm size were kept in a glove box filled with Ar gas where the moisture content and oxygen were controlled below 1 ppm. The prepared electrode was used as a working electrode and lithium foil adhered to copper mesh of 3.0 × 3.0 cm size was used as a counter electrode. An amount of 1 M $LiPF_6$ salt dissolved in a mixture of ethylenecarbonate (EC), ethylmethylcarbonate (EMC), and dimethylcarbonate (DMC) at 1:1:1 volume ratio was used as the electrolyte. The half-cells were assembled in a glove box with Ar atmosphere using polypropylene (PP; Celgard® 2400 microporous membrane) separator to separate the cathode and anode.

Results and discussion

With increasing the amount of oxidizing agent ($(NH_4)_2S_2O_8$), the specific surface area increased and the tapped bulk density decreased significantly due to the increased distance between the graphite layers as shown in Table 1 and Fig. 1. However, the true density, which was measured by the volume of He gas displaced by the sample, decreased significantly at 4 wt% of oxidizing agent, but it increased with the further increase of the oxidizing agent. With increasing the amount of intercalate (H_2SO_4), those properties did not change significantly.

Figure 1 shows the SEM image of natural graphite, EG, and EG composited with petroleum pitch. In the composite, the EG layers were not observed but the carbonaceous composite was globated as the mixture of graphite and pitch. Since the softening point of the petroleum pitch was 250 °C, the pitch would permeate into the gap of EG particles and EG layers, and also encapsulated at the surface of the globated sphere during the heat treatment at 1,000 °C. Figure 2 represents the XRD patterns and Raman spectrums of natural graphite and EGs with different oxidizing agent contents. The 2θ values in XRD of EGs near 26° were almost the same as that of natural graphite but their intensity was much lower. The l_d/l_g (defective/graphitic) values of EGs in Raman were nearly fourfold comparing to natural graphite. These results indicate that the expansion occurred non-uniformly due to the staging effect of the graphite by the intercalate.

The charge–discharge curves of graphite, EG and EG/pitch composite as a function of C-rate are presented in Fig. 3. The left curve shows the charge capability and the right curve is the discharge capability. The EG and EG/pitch composite provide the higher reversible capacity with the more declined curve in the range of 0.05–0.2 V as compared to that of graphite.

Table 2 represents the charge–discharge characteristics of anodes for natural graphite and EGs with different oxidizing agent contents. The discharge capacity and 10 C-rate discharge capability of EG were higher than those of natural graphite reaching 400 mAh/g and 90 %, respectively. However, the initial efficiency of EG

Table 1 Properties of various EGs

Sample	Specific surface area (m^2/g)	Tapped density (g/cm^3)	True density (g/cm^3)
Natural graphite	1.35	0.74	2.26
S600A4T1000	7.3	0.083	0.73
S600A6T1000	8.2	0.042	1.05
S600A8T1000	16.0	0.033	1.21
S600A10T1000	16.2	0.036	1.28
S200A8T1000	19.4	0.034	1.08
S400A8T1000	18.2	0.032	1.26
S800A8T1000	23.2	0.038	1.16

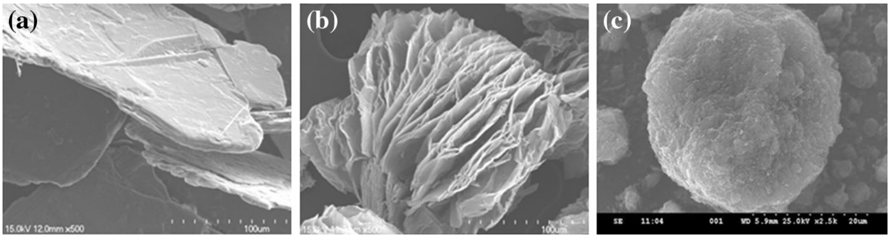

Fig. 1 SEM images of: **a** natural graphite, **b** EG(S600A10T1000), and **c** EG/petroleum pitch composite

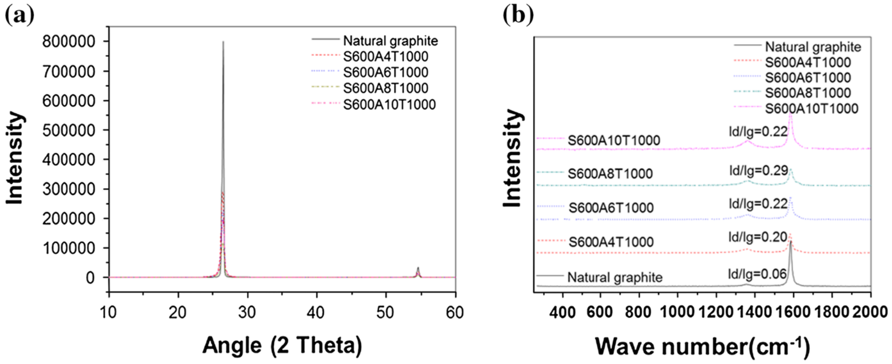

Fig. 2 **a** XRD patterns and **b** Raman spectrums of natural graphite and EGs with different oxidizing agent contents

was lower than that of natural graphite and the EG still had the weak point of potential plateaus for high-power LIB. With increasing the amount of oxidizing agent, the charge/discharge characteristics of EG increased up to 8 wt% and then it decreased with the further increase. From the previous study [10], it revealed that the layer structure of graphite was expanded uniformly allowing the easier intercalation/de-intercalation of Li-ion up to 8 wt% of oxidizing agent but the EG

Fig. 3 Discharge test curve of: **a** natural graphite, **b** EG(S600A10T1000), and **c** P/EG(1:2)

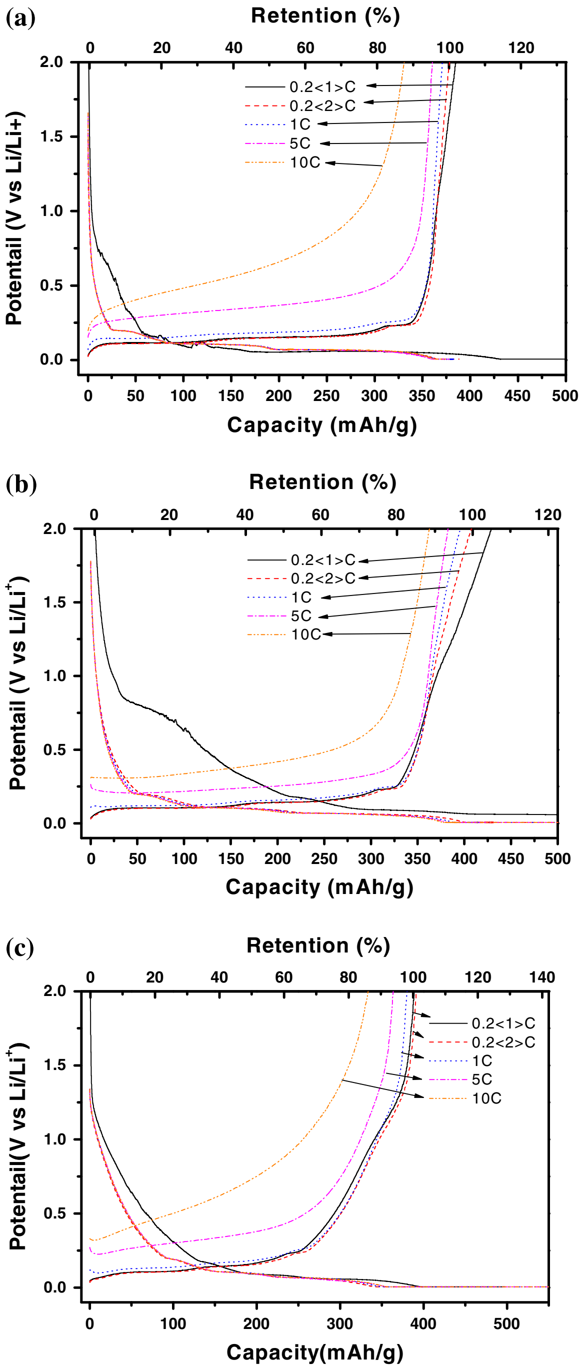

Table 2 Charge/discharge characteristics of natural graphite, petroleum pitch, and EG with different amounts of oxidizing agent and EG/petroleum pitch composites with different mass ratios

Sample	Initial reversible capacity (mAh/g)	Initial efficiency (%)	Discharge rate capacity (%)			Charge capacity (mAh/g)	
			1C	5C	10C	5C	10C
Natural graphite	378	72	98	95	87	19	11
Pitch T1000	286	66	91	83	76	116	–
S600A4T1000	354	63	98	92	87	27	17
S600A6T1000	404	57	97	92	89	51	26
S600A8T1000	410	63	98	95	90	53	29
S600A10T1000	395	57	97	92	85	38	24
P/EG(1:1)	370	68	91	82	71	107	70
P/EG(1:2)	389	78	95	91	82	113	70
P/EG(1:4)	383	79	97	94	92	55	38

with the oxidizing agent content over 10 wt% showed the lesser charge/discharge characteristics due to the excessively widened distance of graphite layer.

In order to solve the problems of potential plateaus and low initial efficiency, the expanded graphite was composited with the petroleum pitch. The composites were prepared by mixing the EG with 10 wt% of oxidization agent and the petroleum pitch at different mass ratios of 1:1, 1:2, and 1:4. The potential plateaus disappeared gradually with increasing the petroleum pitch content as shown in Fig. 2c, and improved charge capacity was also obtained in the composites with the higher petroleum pitch contents as shown in Table 2. However, the initial efficiency and 10 C-rate discharge capability improved with decreasing the petroleum pitch content. Therefore, after considering all the electrochemical properties, the EG/petroleum pitch composite ratio at 2:1 was selected as the optimal condition. It showed an improved initial efficiency of 78 % and the definitely decreased potential plateaus maintaining 389 mAh/g of the initial reversible capacity.

Conclusions

The EG was prepared and applied as anode material for high-power LIB. By changing the processing conditions of EG, a series of EGs with different structures were produced with the changed electrochemical properties. By using different amounts of ammonium peroxodisulfate as the oxidizing agent and changing the heat treatment temperature, the behavior of the intercalation compound (H_2SO_4) and the chemical interaction at the surface and the gap of graphite layers were influenced with the complex change in the EG structure.

The charge/discharge test showed that the initial reversible capacities of the EG anode were around 400 mAh/g and the charge capacity at 5 C-rate was 83 mAh/g. Although these values demonstrated the improved electrochemical properties as compared with those for the natural graphite anode, 378 and 19.4 mAh/g, the EG anode still had some weak points for the high-power anode materials, such as low initial efficiency around 60 % and potential plateaus with the stage characteristic.

In order to solve the problems of potential plateaus and low initial efficiency, the expanded graphite was composited with the petroleum pitch. The anode composite with high performance could be prepared by mixing the expanded graphite with 10 wt% of oxidization agent and petroleum pitch at the ratio of 1:2. This showed an improved initial efficiency of 78 % and the definitely decreased potential plateaus maintaining 389 mAh/g of the initial reversible capacity. By the fabrication of composites with EG and petroleum pitch, the anode material showed an improved initial efficiency and potential plateaus characteristic, exhibiting the possibility of EG anode material for high-power LIB.

Acknowledgment This work was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (MEST) (2010-0025033).

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