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Characterization of silicon- and carbon-based composite anodes for lithium-ion batteries

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Abstract

In recent years development of active materials for negative electrodes has been of great interest. Special attention has been focused on the active materials possessing higher reversible capacity than that of conventional graphite. In the present work the electrochemical performance of some carbon/silicon-based materials has been analyzed. For this purpose various silicon-based composites were prepared using such carbon materials as graphite, hard carbon and graphitized carbon black. An analysis of charging–discharging processes at electrodes based on different carbon materials has shown that graphite modified with silicon is the most promising anode material. It has also been revealed that the irreversible capacity mainly depends on the content of Si. An optimum content of Si has been determined with taking into account that high irreversible capacity is not suitable for practical application in lithium-ion batteries. This content falls within the range of 8–10 wt%.

The reversible capacity of graphite modified with 8 wt% carbon-coated Si was as high as 604 mAh g^{-1}. The irreversible capacity loss with this material was as low as 8.1%. The small irreversible capacity of the material allowed developing full lithium-ion rechargeable cells in the 2016 coin cell configuration. Lithium-ion batteries based on graphite modified with silicon show gravimetric and volumetric specific energy densities which are higher by approximately 20% than those for a lithium-ion battery based on natural graphite.

Keywords: Lithium-ion battery; Natural graphite; Silicon; Hard carbon; PUREBLACK® carbon

1. Introduction

Lithium-ion batteries (LIBs) with high energy density are in great demand as energy sources for many applications. In the modern commercial lithium-ion batteries graphite is mainly used as a negative active material [1,2]. Graphite provides a theoretical capacity of 372 mAh g^{-1}, which limits the specific energy density of LIBs. Further improvement of LIBs would become possible with the use of new electrode materials with a higher specific volumetric capacity. Therefore, developing alternative anodes for lithium-ion batteries has been of great interest recently. Various materials (such as Si, Sn, Al [3–6], metal oxides [7–9], hard carbons [10–13], etc.) capable of the reversible lithium storage were investigated for the purpose of increasing the specific capacity of negative electrodes.

Anodes based on silicon are a very attractive alternative to graphite, because silicon can electrochemically form alloys with lithium, allowing a composition of up to 4.4 Li per Si, which potentially yields an extremely large theoretical specific capacity of 4200 mAh g^{-1} [14–16]. The main drawback of these electrodes is very poor cycling life. A huge change (of about 300%) in volume that occurs during the lithium alloying and dealloying processes results in mechanical crumbling of the electrodes [2,10,17]. Considerable efforts have been made to reduce the irreversible capacity and fading of the capacity of the electrode upon prolonged cycling. Some recommended methods are as follows:

(i) Development of electrodes obtained by deposition of silicon-based films of different types onto the current collectors [18–23]. Nevertheless, it is well known that the capacity of an electrode mainly depends on the active materials loading. The above electrodes had a thickness of silicon that lay within the range of several hundred nanometers, while in practice current collectors had a minimum

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thickness of dozens and hundreds microns. Therefore, the total specific capacity of such electrodes was several times as low as the specific capacity of commercial electrodes based on graphite.

(ii) Development of some composite materials where Si is dispersed homogeneously within an electrochemically inactive matrix [24–26]. The electrochemically inactive phase is preferred to be comprised of a soft and ductile matrix of quite sufficient volume (60–70%), which can compensate mechanical stresses/strains by the active Si-based phase. As a result, structural integrity of the composite electrode can be retained during the alloying and dealloying processes. On the other hand, different changes in the volume of silicon and inactive matrix may bring a mechanical stress at the interface and results in disconnection between Si and the inactive matrix. Such structural instability could be especially considerable in the initial cycles, causing a higher irreversible capacity.

(iii) Reduction of the particle size of silicon into the nanometer range provides better cycling behavior due to reduction of the mechanical stress during lithiation of silicon. Combination of this factor with developing the composite material where nano-sized Si is dispersed homogeneously within some electrically conductive and also electrochemically active matrix (like graphite or carbon matrix) is the most promising for practical application in LIBs. Several authors [27–29] reported that such materials showed a very high reversible capacity. As a rule, such Si-based composite materials show not only quite high first discharge and charge capacities (400–3000 mAh g^{-1} depending on the content of Si), but also a high irreversible capacity, which is not suitable for the practical commercial applications in LIBs.

The present study has been aimed at characterizing and optimizing some silicon/carbon composites as well as at estimating a possible practical effect for their application in LIBs. In this study the authors have focused on the application of silicon-based composites which exhibit a high reversible capacity and good capacity retention along with a lower irreversible loss in the first cycle. Results of the study are presented below.

2. Experimental

2.1. Materials preparation

The Formula BT^{TM} SLA1025 and its modification with carbon-coated Si (denoted in the paper as SLA1025/Si/C) and PUREBLACK®205-110 carbon (a new material on the battery market, best described as nano-sized partially graphitized carbon black) were used in the investigation. All the above materials were commercial products of Superior Graphite Co., Chicago, IL, USA.

The hard carbon was prepared from table sugar by the method described in Ref. [30]. Sugar precursor (“sulfuric acid washed” sugar) was pyrolyzed at 1273 K for 3 h in a high-purity argon atmosphere (99.95% Ar) using a heating rate of 5 K min^{-1} and a flow rate of 100 ml min^{-1}.

The as-received Si powder (99.9%, Aldrich), which will be referred to as the 20 μm powder, was ball-milled in a polypropylene jar that contained two different tungsten carbide balls (6 mm and 3 mm in diameter). The milling was conducted for 24 h with a rotation speed of 300 rpm. The particles of Si after milling were in the range 2–3 μm.

The composite materials such as graphite/Si, hard carbon/Si and PUREBLACK®/Si were prepared by mixing elementary powders of silicon and carbon materials. The mixing was carried out during 24 h in a Y mixer (so-called zig-zag mixer) filled with argon in order to prevent any oxidation of the reactive components during the mixing. In the Y mixer the process involves separation of the powder into two flows followed by turbulent mixing as the mixer is inverted quickly with a pause to allow the powder to move down a Y-type tube. This method of preparation was selected in order to avoid the formation of inactive SiC and amorphization of graphite, which often occurs during the preparation of composite by ball milling of carbon and Si [31].

In this work commercial grade lithium cobalt oxide manufactured by LICO Technology Corp. (available through Pred Materials International Inc., of New York, NY, USA) was used. The commercial grade L210 was selected for investigation and design of a lithium-ion battery.

2.2. Electrochemical characterization

The active materials were mixed with the amount of 7–9 wt% polyvinylidene fluoride (PVDF) in *N*-methylpyrrolidine (NMP) solution. The resulting slurry was cast onto a metal foil, and a doctor blade with a gap opening of 200 μm was used to define the maximum thickness of the freshly coated layer. The resulting film was dried at 120 °C in order to evaporate the NMP. The electrodes were compacted to the desired density by calendering. The active loadings of the anode and cathode were in the range of 6–12 mg cm^{-2} and 15–30 mg cm^{-2}, respectively. The thickness of the electrodes was monitored with a Mitutoyo (Japan) micrometer. The thicknesses of the active layers of electrodes were in the range 0.08–0.10 mm. The average density of the graphite layer ranged between 1.4 g cm^{-3} and 1.6 g cm^{-3}. The average density of cathode layer was in the range 2.3–3.2 g cm^{-3}. The disc electrodes having a diameter of 16 mm were cut out of the coating film cast onto metal foil current collector using a punch. Before assembling the cell the electrodes were dried under a primary vacuum at 120 °C in the time frame of 12 h. The coin cells (CR2016 standard size) were assembled in an argon-filled glove box (Unilab model, MBraun, USA). The TEKLON^{TM} EDEX separator (manufactured by ENTEK Membranes LLC, USA) and the electrolyte (1 M $LiPF_6$ in a 1:1 volume mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) provided by MERCK, Germany) were used for assembling the coin cells. Electrochemical investigations were performed using a 32-channel battery cycler MSTAT 32 from Arbin Instruments, USA.