

Microstructure control of the graphite anode with a high density for Li ion batteries with high energy density



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ABSTRACT

As the density of graphite anode is increasing, the pore size and volume in the graphite anode is reduced, which results in a decrease in the electrolyte permeability of electrode. The electrochemical degradation of high density graphite anode due to the low permeability is a major obstacle to its use as anode for lithium ion batteries. In this study, we report on high density graphite anode with the carbon additive added that provides micron size pore structure of the high density graphite anode, which results in an increase in the rate capability. The high density graphite anode with carbon additive exhibited 32.4% higher rate capability at 1 C compared to the high density graphite anode without carbon additive. This improvement is mainly attributed to the increased micron-size pores, which enhances the kinetic associated with lithium by improved electrolyte permeation and increased interface between the electrolyte and active material.

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1. Introduction

Rechargeable lithium ion batteries (LIBs) have been considered as one of the most attractive energy storage choices for electric vehicles, cellular phones, and lap-top computers due to their high energy and power density [1–7]. The existing challenge in LIBs is to increase the energy density to expand their application fields. There are two general approaches to increase the energy density of LIBs. For the case of anode, one approach is to use an alternative material to replace typical graphite anode such as silicon because of the inherent large theoretical energy density [8–10]. However, poor cycle performance caused by large volume expansion associated with lithiation/delithiation (~400%) during cycling limits its practical use [11–13]. The other approach is to increase the density of graphite anode [14–17]. By increasing the electrode density from 1.5 g/cm³ (low density graphite electrode) to 1.8 g/cm³ (high density graphite electrode), the capacity of common 3000 mAh cell can be increased to 3600 mAh under

similar volume conditions. Hence, the average change of the capacity is ~200 mAh per an electrode density of 0.1 g/cm³. However, there exist some challenging issues for applying the high density graphite anode to LIBs. After the pressing process in due course of high density graphite anode preparation, the pore size and volume in high density graphite anode were significantly reduced. The effect of electrode density on cycle performance and irreversible capacity loss for natural graphite anode in LIBs was reported [18]. And only a few researches try to address these problems by applying active materials coated with an expensive conducting material for high density electrode [16,19].

In this study, from a different but an important point of view, we analyzed the role of micron-size pore structure in the high density graphite anode to improve the electrochemical properties. We introduced highly conducting carbon additive to the high density graphite anode to control the pore size/density and electronic conductivity. The carbon additive enables micron-size pores and enhanced electronic conductivity in the high density graphite anode which improves kinetics associated with both lithium ion and electron by enhancing electrolyte permeation and increasing Li ion flux at the interface between the electrolyte and active material [20]. The high density graphite anode with carbon

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additive exhibits significant improvements in electrochemical properties including the rate capability, reversible capacity and cycle performance.

2. Experimental

2.1. Evaluation of electrochemical properties

To prepare the high density graphite electrodes with and without carbon additive, graphite as active materials, denka black as carbon additive, carboxymethyl cellulose (CMC) and styrene butadiene rubber (SBR) as a binder were used in a weight ratio of 97.5: 0: 1: 1.5, 96.5: 1: 1: 1.5, respectively. The mass loading of both samples is 13.8 mg/cm^2 . The mixing process was conducted by Thinky mixer at 2000 rpm for 10 min. The prepared slurry was coated onto a copper current collector by doctor blade to make electrodes and dried for 6 h in a vacuum oven at 145°C . Coin-type full cells (2032 R type) were fabricated to evaluate the electrochemical properties of the high density graphite electrode with and without carbon additive. LiCoO_2 was used as the cathode electrode which electrode density is 4.1 g/cm^3 after drying for 6 h in a vacuum oven at 110°C . 1.7 M LiPF_6 in ethylene carbonate/diethyl carbonate/ethyl-methyl carbonates (EC/DEC/EMC, 1: 1: 1 vol%, PANAX StarLyte) was used as the electrolyte. The coin-type full cells were cycled at a rate of 0.1 C between 3 and 4.3 V using a battery cycle tester (TOSCAT 3000, Toyo Systems, Tokyo, Japan)

2.2. Characterization

The high density graphite electrode with and without carbon additive were characterized using a field emission scanning electron microscope (FE-SEM, JEOL JSM-7600F), Mercury Porosimetry (Micromeritics Instrument Corporation, AutoPore IV 9500 V1.07), and Penetration tester (Pnt-n peneto analyzer, Hosokawa micron corporation)

3. Results and discussion

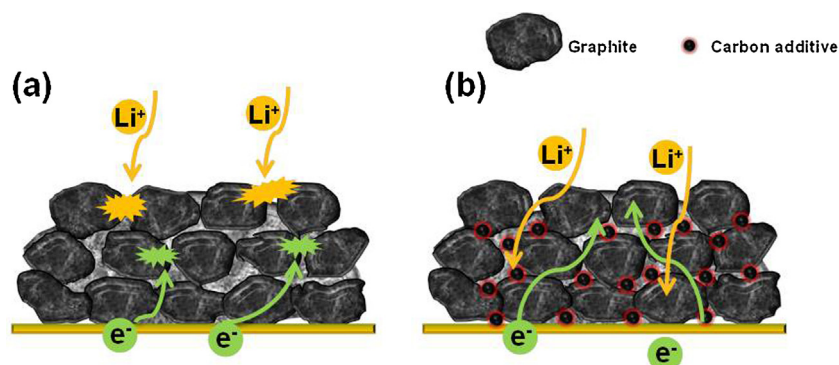
Our preliminary experimental results showing the top view SEM images of graphite electrodes with different densities (1.5 g/cm^3 – 1.8 g/cm^3) clearly reveal significant decrease of the pore size and volume in the graphite electrode with the increase of the electrode density (Fig. S1), which is confirmed by mercury porosimetry in Fig. S2. The graphite electrode with the electrode density of 1.9 g/cm^3 exhibits 17.3% lower porosity compared to that of the graphite electrode with the electrode density of 1.6 g/cm^3 (45.8%). (Table S1) The low electrode porosity in the graphite anode with a high energy density results in poor electrolyte penetration

(Fig. S3), which consecutively leads to poor lithium ion diffusivity (Fig. S4, Table S2). These results indicate that both the poor electrolyte penetration and the low porosity are the major causes for the poor electrochemical properties. Therefore, the pore system including size, density and distribution in high density graphite electrode should be considered as a dominant factor to improve the electrochemical properties.

Scheme 1 shows the schematic illustration for the Li ion diffusion and electron conduction in the high density graphite anode without and with carbon additive. In the high density graphite anode without carbon additive, the electrolyte is hard to penetrate into the high density graphite as it is totally blocked by highly pressed graphite active materials. However, in the high density graphite anode with carbon additive, the carbon additive could generate locally large pores (micron-size) in the interior of the electrode and increase the surface area of the electrode, which enables the improvement in kinetics associated with lithium by the facile electrolyte penetration as well as large Li ion flux at the interface between the electrolyte and active material.

The microstructures of the high density graphite electrodes with and without carbon additives were observed by scanning electron microscopy (SEM). (Fig. 1) The detailed information on both electrodes is described in the Table S3. As shown in Fig. 1 (a)–(d), the high density graphite anode without carbon additive exhibits a dense configuration. In the high magnification SEM image, the active materials are densely packed without large gap or pore. Even though the high density graphite anode with carbon additive exhibits densely packed configuration, large gap and pore are clearly observed in the electrode. This phenomenon is also observed in the cross sectional SEM images. (Fig. S5). Although the excessive pore and large pore size could increase electrical resistance, the high density graphite anode with carbon additive shows higher electronic conductivity compared to that of the high density graphite anode without carbon additive. After some cycling of the graphite electrode, small gap between the graphite particles could be generated even after severe pressing process of the electrode due to the volumetric change of the graphite electrode associated with Li ion as shown Fig. S6. The disconnection between graphite particles results in poor electronic conductivity of the electrode as well as the degradation of cycle performance. By introducing the carbon additive into the graphite electrode, the disconnection between graphite particles could be reduced via filling the gaps by carbon additive. As shown Fig. S7, the graphite anode with carbon black exhibits much higher electronic conductivity (6.20 S/cm) compared to that of the graphite electrode without carbon black (2.33 S/cm).

To analyze the pore volume and size distribution of high density graphite anode with and without carbon additive, mercury



Scheme 1. Schematic illustration of (a) the high density graphite anode without carbon additive and (b) the high density graphite anode with carbon additive.

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