

Thermal behavior of Graphite and Si anode for lithium-ion batteries.

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Abstract : The thermal reactivity of graphite and silicon anode materials at elevated temperature is investigated by differential scanning calorimetry (DSC). For DSC measurements, lithiated Graphite and Si anodes are heated in a hermetically sealed high-pressure pan with a polyvinylidene fluoride (PVDF) binder and a 1 M LiPF6 solution in an ethylene carbonate (EC)-diethyl carbonate (DEC) mixture. It is founded that the particle size has a strong influence on the thermal stability of the lithiated graphite and silicon anodes. The heat generation due to the solid electrolyte interface (SEI) decomposition increases with decreasing the particle size. The onset temperatures for exothermic reactions after initial SEI decomposition appear to be lower for electrodes with smaller particle sizes. Carbon coating on the spherical natural graphite also enhances the thermal stability of the natural graphite electrode.

Key words : Lithium-ion battery, Anode, Thermal stability, DSC, Particle size, Carbon coating

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1. INTRODUCTION

The safety-related performance of lithium ion batteries is a major concern in their high-power battery applications such as hybrid electric vehicle (HEV) and electric vehicle (EV) propulsion. The safety of lithium-ion batteries is closely related to the thermal stability of the cell materials.

It is also known that the thermal stability of anode is critical to the thermal runaway of lithium-ion batteries.[1),2)]

According to previous studies using DSC[3)-5)] and accelerated rate calometry (ARC)[6)], the thermal reactions of electrodes are dependent on many factors such as the active material, state of charge, binder level, the presence of electrolyte and so on. However, little attention has been paid to the effect of particle size of graphite and Si powders on the thermal stability of graphite and Si anodes. Surface modification by carbon coating the graphite surface has been reported as an effective approach to suppress the irreversible intercalation of the solvated species and the side-reactions leading to the formation of the SEI layer.

Thus, It is necessary to evaluate effect of particle size and carbon coating on the thermal stability of spherical natural graphite at elevated temperature.

In this work, we investigated the thermal stability of lithiated flake-type graphite and silicon with different particle sizes when heated in 1.0M $LiPF_6$ EC/DEC electrolyte. The effect of carbon coating on the thermal stability of spherical natural graphite is also examined using unmodified and carbon-coated natural graphite spheres of similar shape and particle size.

2. EXPERIMENTAL

2.1 Material preparation

2.2.1 Particle Size effect

The graphites used in this study were four natural graphites with different sizes. These graphite samples had particle size distributions that peak at 3.6, 5.7, 25.4, and 138.4 μm. We call these samples G1, G2, G3 and G4.

Si powders with different particle sizes - S1 (15 μm, 99%, Aldrich), S2 (5 μm, 99.9%, High Purity Chemicals), S3 (30 – 50 nm, 98%, Nanostructured & Amorphous Materials, Inc.) – were used.

2.2.2 Carbon Coating effect

Unmodified natural graphite and the carbon-coated natural graphite samples were used as provided by Poscochemtech, Inc.,Korea. Both graphite samples have similar shapes and particle sizes.

2.2 DSC analysis

For DSC analysis, the cells were pre-cycled three times to reach a stable capacity level and the cycling was interrupted when the cells were charged to a fully intercalated state. The charged cells were disassembled in a glove-box. Discs with a diameter of 0.5cm and a copper current-collector were cut from the electrode sheet without removing the electrolyte and transferred to a high-pressure stainless-steel pan with a gold-plated copper seal. The DSC scans were performed with a DSC 200 F3 instrument (NETZSCH, Germany) at scan rate of 10 °C min^{-1}

3. RESULT AND DISCUSSION

3.1 Particle size effect

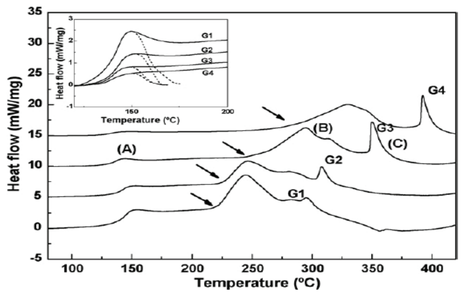

Fig. 1 DSC profiles of four graphite electrodes in fully lithiated state with electrolyte at scan rate of 10 °C min^{-1}.

All samples show similar heat evolution characteristics. It typically consists of three heat evolution peaks designated as A, B, and C for all of the samples. However, it appears that there are some distinct differences in the amounts of heat evolved and the positions of exothermic peaks, in which the peak B and C shift to higher temperature with increasing particle size. The amount of heat evolved at around 150 ◦C was determined from the dotted line curves in inset of Fig. 1. The peak area increases with the irreversible capacity loss in the first cycle, and is closely related with BET surface area. The onset temperature for main heat generation above 200 ◦C, due to the reaction of the lithiated graphite with PVDF and/or electrolyte, also moves to a higher temperature with an increase in particle size. As the particle size of graphite decreases, more lithium becomes available for the reaction at lower temperatures due to the reduced diffusion path and higher surface area.

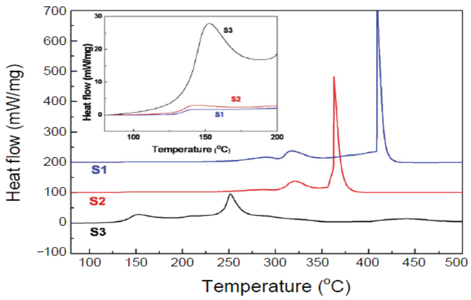

Fig. 2 DSC curves of fully lithiated Si electrodes with different particle sizes.

As shown in the inset of Fig. 2, the thermal evolution at approximately 140℃ increases with decreasing particle size for fully lithiated Si electrodes. Since the thickness of a solid electrolyte interface (SEI) layer on an Si film anode increases with lithiation and more SEI film is formed in the electrode with a smaller particle size, it is suggested that the thermal evolution at approximately 140 °C is mainly due to the thermal decomposition of the SEI film. The major exothermic peak is significantly reduced and shifted to the lower temperature side as the Si particle size decreases. This may be because the reduced diffusion path and larger surface area in smaller Si particles facilitate the evolution of lithium at lower temperatures, resulting in an exothermic reaction with electrolyte.

3.2 Carbon coating effect

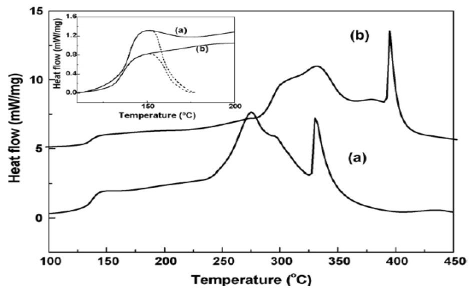

Fig. 3 DSC curves of (a) unmodified and (b) carbon-coated NG electrodes in fully lithiated state at scan rate of 10 °C min^{-1}.

The exothermic peak due to the initial SEI film decomposition is illustrated as the dotted line curves in the inset of Fig. 3. The estimated heat generation of the unmodified NG is 240 J g^{-1}. Surprisingly, the carbon-coated NG shows a lower heat generation of 144 J g^{-1}, which is 40% less than from the unmodified NG.

The major exothermic peak is reduced and shifted to the higher temperature side as the carbon coating effect. It is seems to be that the carbon coating layer suppresses the release of intercalated lithium from NG at high temperatures and protects the graphite structure from electrolyte attack.

4. CONCLUSION

The effect of particle size of the graphite and silicon on the thermal behavior of fully lithiated natural graphite anodes has been investigated using DSC.

The heat evolved at temperatures below 200 ◦C, mainly due to the SEI decomposition and the reaction of the intercalated lithium with the electrolyte, increases with decreasing the particle size. This is attributed to the amount of SEI film formed during precycling, as inferred from the initial irreversible capacity. As a result of the letter, the onset temperature for main heat generation above 200 ◦C, due to the reaction of the lithiated graphite and silicon with PVDF and/or electrolyte, also moves to a higher temperature with an increase in particle size. The thermal stability of the graphite and silicon anode depends on the particle size of active material.

Carbon coating on the spherical natural graphite also enhances the thermal stability of the natural graphite electrode. It is confirmed by DSC and XRD analysis that the carbon coating layer suppresses the release of intercalated lithium from NG at high temperatures and protects the graphite structure from electrolyte attack. This supports the conclusion that a carbon coating on NG improves the thermal stability of unmodified NG.

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