Short communication

A study of the surface morphology of a disordered carbon electrode

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Abstract

The change in the morphology of a discharged disordered carbon electrode surface is observed using atomic force microscopy (AFM). It is found that a stable film with a 'hill-like' structure is formed on the surface after the first charge and discharge processes. The thickness of the film is between 60 and 200 nm. The film is much thicker than that formed on the surface of either a lithium metal anode or a graphite electrode. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

It is well-known that an irreversible capacity loss (ICL) is produced in lithium-ion rechargeable batteries (LIBs) during the first cycle because of side reactions. That is, lithium charged into the carbon electrode cannot be discharged from the carbon electrode. The lithium supply in a LIB comes from the cathode when the cell is manufactured and thus in order to compensate for the loss of lithium which is irreversibly consumed, an excess of cathode material needs to be used. As a result, the specific energy of the cell decreases and the cost increases.

In order to understand and decrease the ICL, many studies of the mechanism of the charge and discharge processes have been reported [1–3]. The ICL has been attributed to reductive decomposition of the solvent followed by the formation of a Li-ion conducting, solid electrolyte interphase (SEI) on the surface of the anode. The SEI thus produced can suppress further decomposition of the solvent. Therefore, after the first cycle, there is never a direct and free contact between the carbon anode and the electrolyte solution. The electrochemical reactions take place at the interphase between the SEI and the

electrolyte solution. Thus, the performance of the anode depends strongly on the properties of the SEI [4].

Recently, Inaba et al. [5], using in-situ scanning tunnel microscopy (STM), found, that two kinds of hill-like structure (8–10 Å in height) are present on the surface of highly oriented pyrolytic graphite (HOPG) when such material is used as an anode. They attributed the topographical change in the anode to the intercalation of solvated lithium ions. Hirasawa et al. [6] reported an in-situ electrochemical study with atomic force microscopy (AFM) of the change in morphology of the HOPG surface. After the potential of the sample was stepped to below 0.9 V (Li/Li$^+$), a thick SEI with island-like structures was observed. The SEI had a minimum thickness of 50–70 nm and was much thicker than that formed on the surface of a lithium metal anode [7]. To our knowledge, although the morphology and thickness of the SEI formed on the HOPG surface have been examined, there have been no published investigations of the surface morphology and the thickness of the SEI formed on a disordered carbon electrode.

It is well-known that the ICL displayed by a disordered carbon electrode during the first cycle is larger than that produced by a graphite electrode. Therefore, in order to understand the ICL and improve the performance of the LIB, it is very important to obtain information on the surface morphology of the disordered carbon electrode after the first cycle. The present work is aimed at investigating the surface morphology of the discharged disor-

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dered carbon electrode and measuring the thickness of the SEI by AFM.

2. Experimental

In order to observe the morphological change on the carbon electrode surface, it is necessary to select an available carbon electrode material. HOPG is useful as a model compound for the graphite electrode in the LIB since it has a flat surface. In this work, a ribbon-like carbon film (RCF) was used as the model compound for the disordered carbon electrode since it has a relatively flat surface and the structure of a disordered carbon. The crystallite size, L_c, and the interlayer spacing of the RCF are 16 and 3.48 Å, respectively [8]. The crystallites are randomly distributed according to the results of a pole figure measurement [8]. An RCF of 10 μm thickness, 10 mm width, and 15 mm length was used as the anode. A lithium sheet and a lithium chip were used as the counter and reference electrodes, respectively. One-third of the pristine RCF was put into the electrolyte solution and the two-thirds were kept above the surface of this electrolyte solution so that a boundary between part of the pristine RCF and that of the discharged RCF could be formed after the first cycle, as shown in Fig. 1. The discharged RCF was obtained using 1 M LiClO$_4$ propylene carbonate electrolyte with a three-electrode cell in an argon glove box. The pristine RCF anode was charged to 0.01 V (Li/Li$^+$) and discharged to 2.0 V (Li/Li$^+$), then kept at 2.0 V until a steady current was reached (10^{-5} to 10^{-6} A). The discharged RCF was rinsed with propylene carbonate to remove the electrolyte and dried in a vacuum. The discharged RCF was directly examined by AFM.

In order to perform an AFM observation, the sample was fixed with double-sided adhesive tape to the top of a stand. AFM images were obtained using a Nano III microscope (Digital Instruments). All measurements were conducted at room temperature in air.
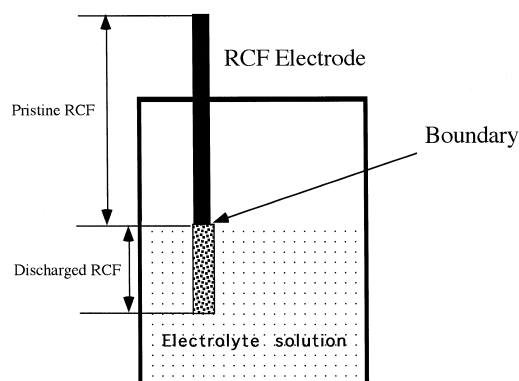

Fig. 1. Schematic representation of the boundary between part of the pristine RCF and that of discharged RCF.

3. Results and discussion

A typical AFM image of pristine RCF is shown in Fig. 2. There are many ridges and furrows on the surface of the RCF, (Fig. 2a). These ridges have a regular direction and their heights are quite similar. This surface morphology may be a result of the special preparation process. The mesophase pitch was melted and spun through a slit-shaped nozzle to form a continuous precursor RCF, and clearly the surface of the nozzle would exert a large effect on the surface morphology. The fine features of smaller ridges and furrows have the same characteristics (Fig. 2b). The height of these ridges and furrows can be quite accurately estimated by the z range shown in the images and, was in the range of about 1 to 5 nm.

AFM images of discharged RCF are presented in Fig. 3. Although the surface of the pristine RCF has some ridges and a furrow structure, a marked change in morphology be clearly observed after the first cycle. The regular ridges and the furrow structure largely disappears and several 'hill-like' structures develop, see the lower and upper parts of Fig. 3a. It is clear that the size of the hills is larger than 1 μm. There are some irregular ridges in the vicinity of the hills. They have different heights and baselines, and an irregular distribution. A magnified image of the fine features of the hill-like structure is given in Fig. 3b. The hill-like structure on the disordered carbon electrode is similar to the island-like structure, observed by in-situ AFM, on the HOPG [6].

According to our previous work [1], the ICL produced by a disordered carbon electrode is related both to the solvent decomposition on the surface of the electrode and to the reaction of lithium with active sites in the bulk of the electrode [1]. Therefore, based on a comparison of Figs. 2 and 3, it can be postulated that the morphology change of the RCF electrode is due to the SEI formed on its surface through solvent decomposition.

In order to obtain the thickness of the SEI, one of the available methods is to find the boundary between part of the pristine RCF and part of the discharged RCF. As described in the experimental section, it is possible to find the boundary in the area of the one-third discharged RCF. An AFM image of this area is shown in Fig. 4. The lower left corner of this image and that shown in Fig. 2 display the same morphology. Thus, the lower left corner in Fig. 4 is pristine RCF. On the other hand, the upper part of Fig. 4 has a different morphology, and represents discharged RCF. It can therefore be considered that the area between these two regions is the boundary. It is very clear that the boundary is not straight and that 'hill-like' structures appear in the vicinity of the boundary.

The cross-sectional profile of the SEI in the vicinity of the boundary is shown in Fig. 5 and the horizontal and vertical distances between the marks are also shown in the accompanying Table. The region in which the SEI was not formed in the vicinity of the boundary, is indicated by the
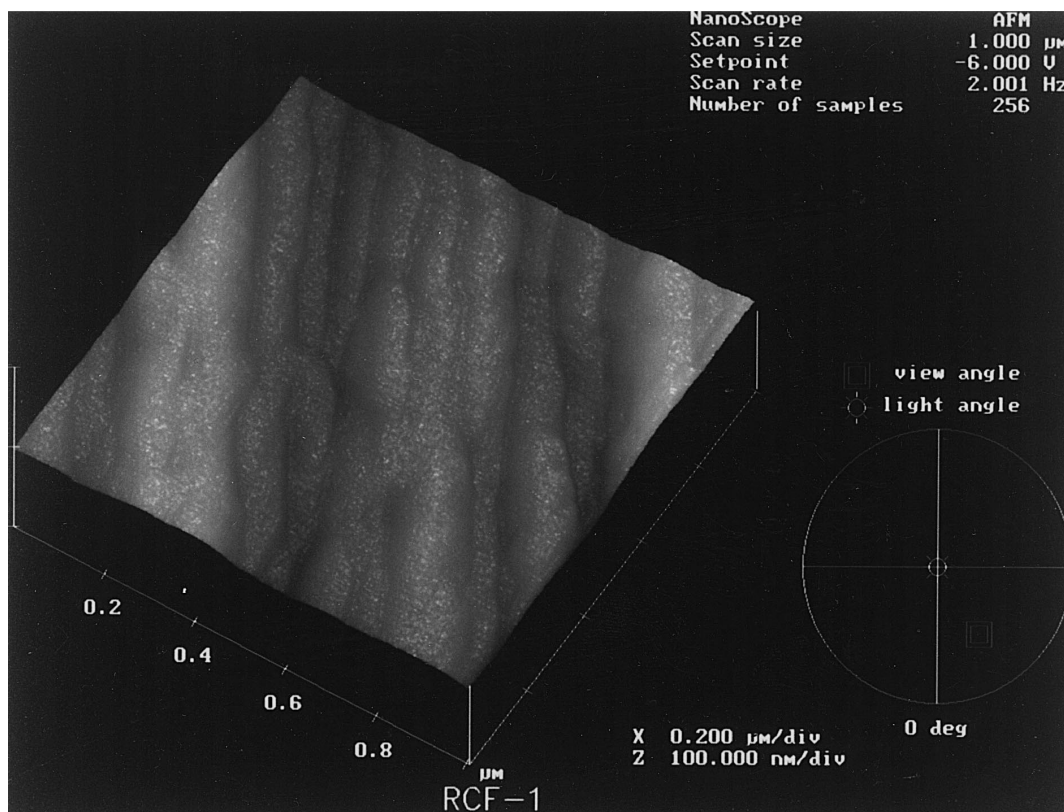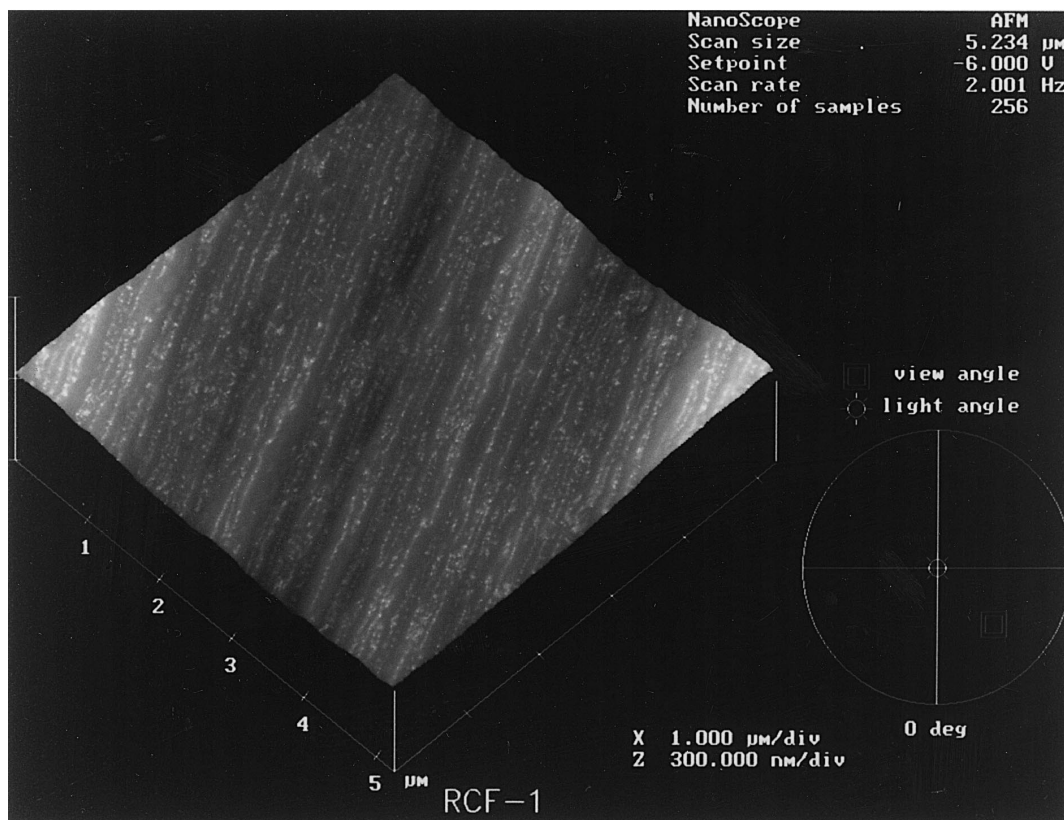
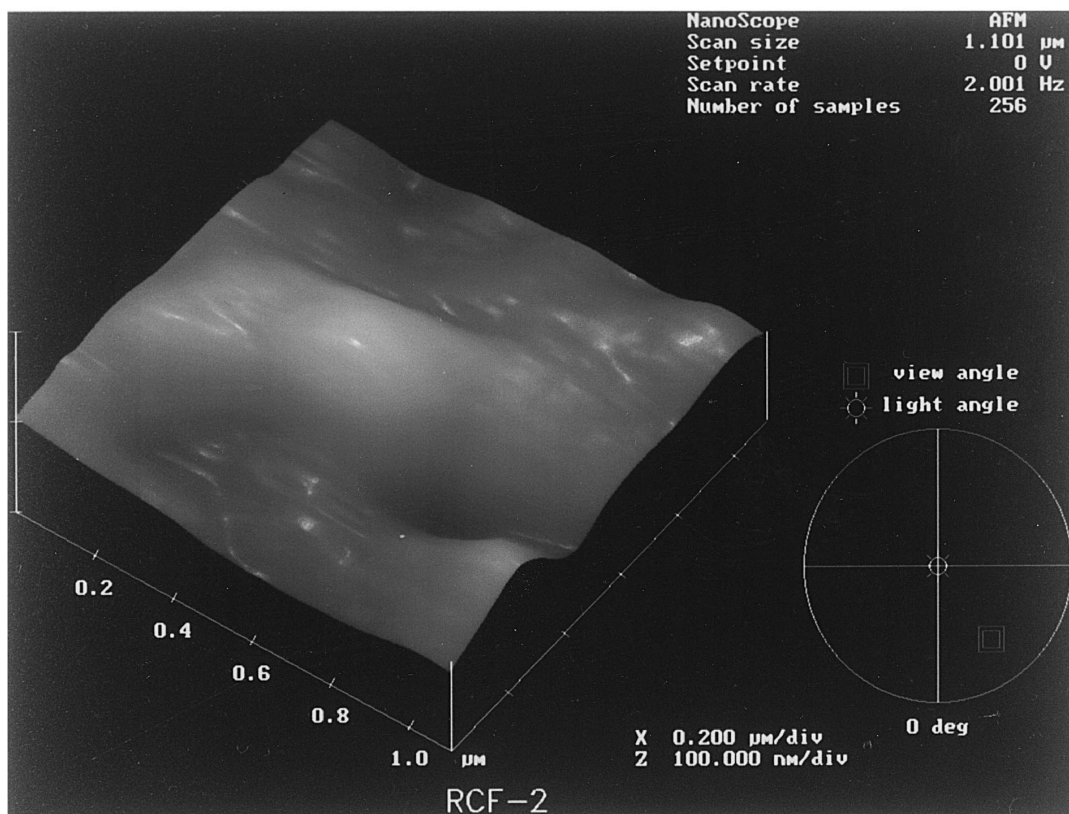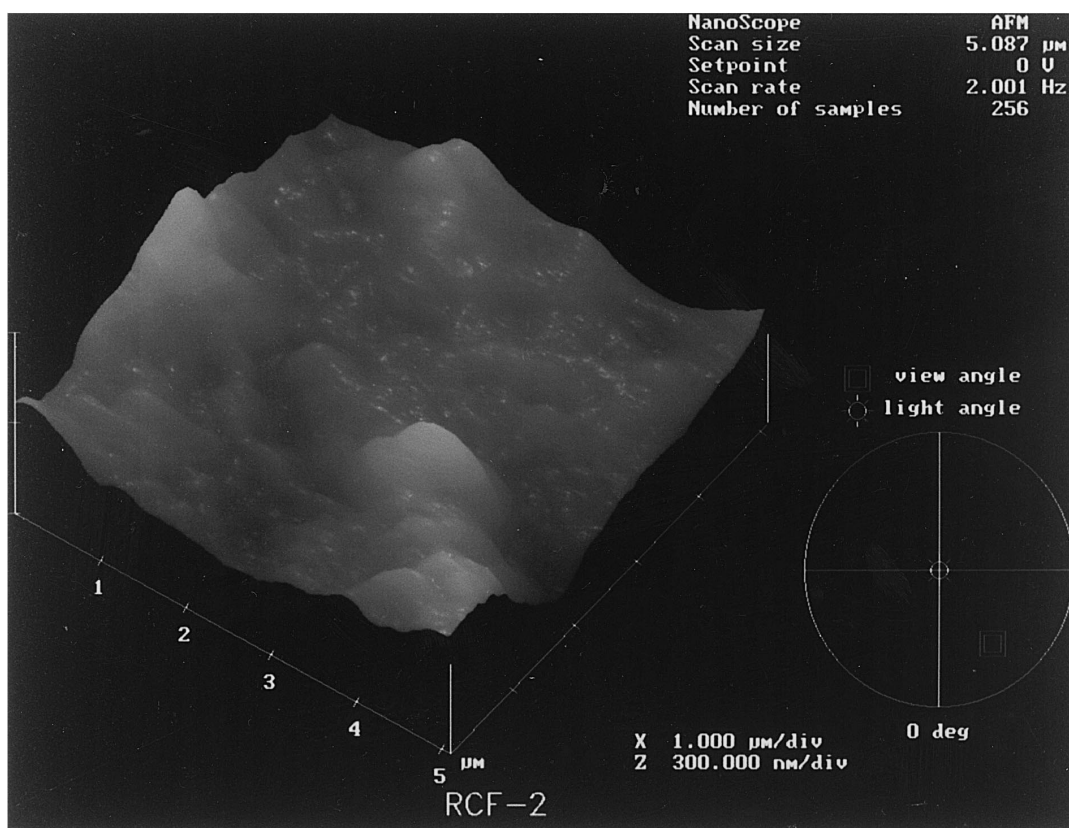Fig. 2. AFM image of pristine carbon anode electrode.

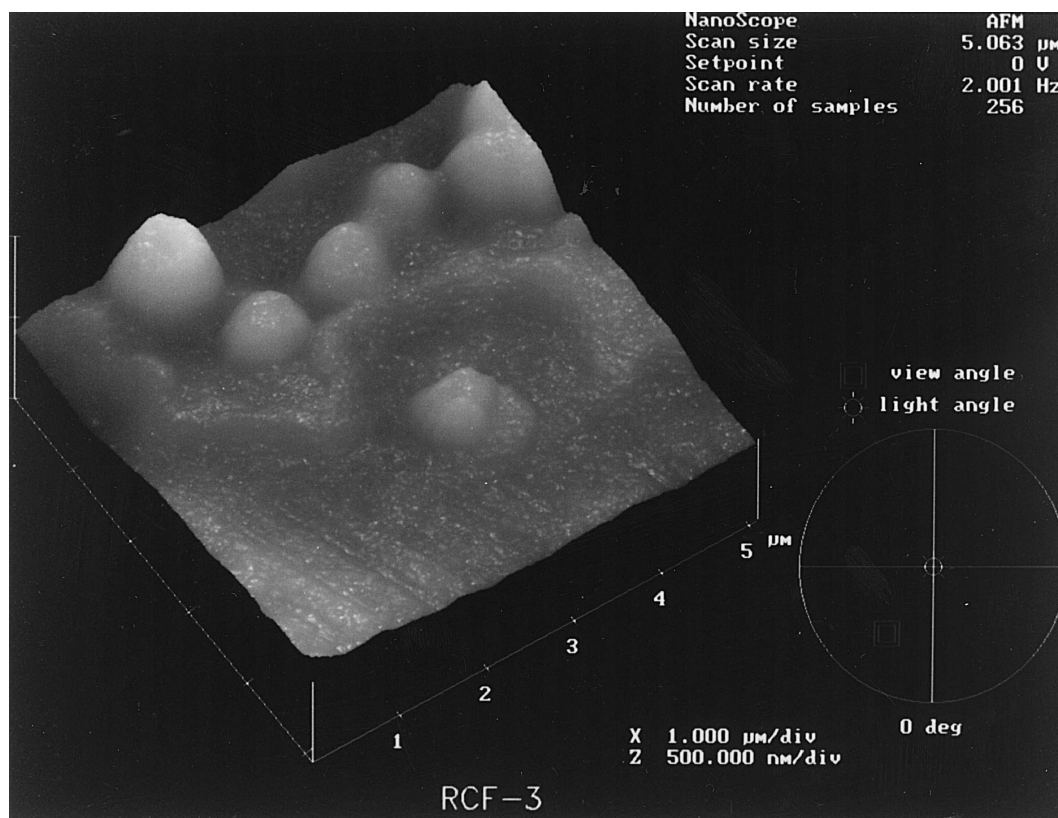Fig. 3. AFM images of discharged carbon anode electrode.

Fig. 4. AFM image of the boundary between the parts of the pristine carbon and discharged carbon.
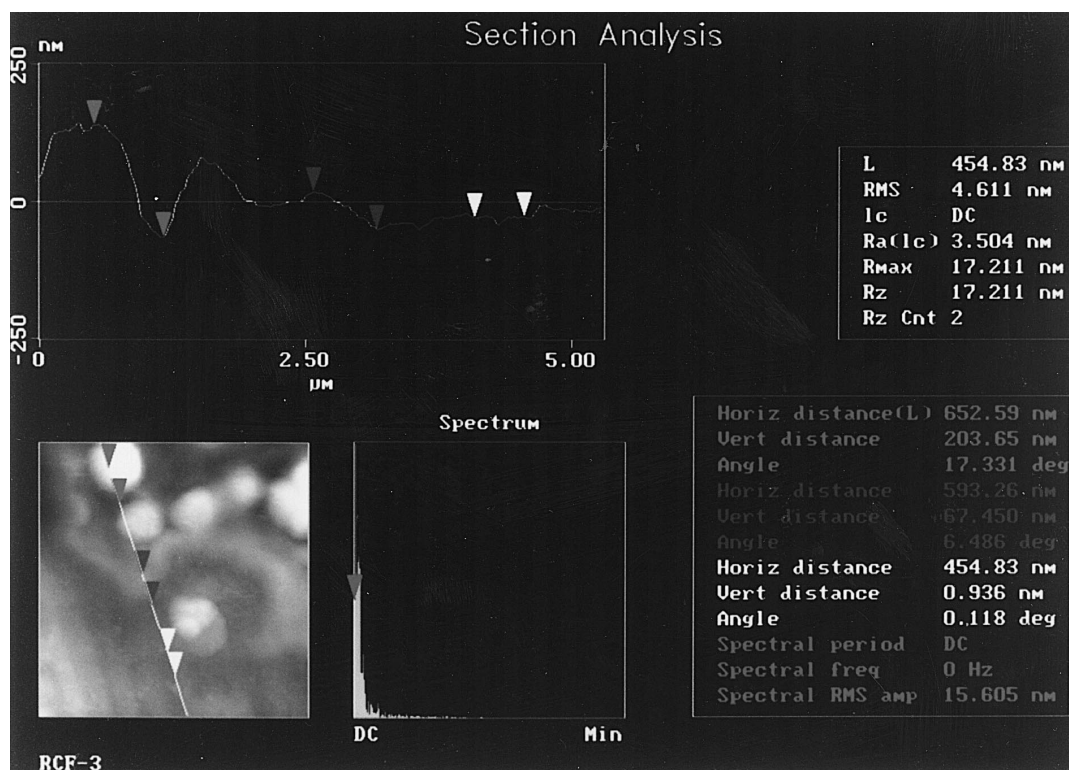

Fig. 5. Cross-sectional profile of the boundary between regions of pristine carbon and discharged carbon; the horizontal and vertical distances between markers are shown in the accompanying Table.

two white arrows in the Fig. 5. Their difference in height is about 1.0 nm. The region of the 'hill-like' structures and the boundary are indicated by the red and green arrows, respectively. The corresponding differences in height between two marks of same colour are 204 and 68 nm, respectively. This means that the thickness of the SEI is about 68 nm, but the height of the hill on the SEI is ~ 136 nm. It is considered that the thickness of the SEI on the surface of the disordered carbon electrode is in the range of 68–204 nm.

The thickness of the SEI formed on the disordered carbon electrode is much thicker than that formed on the lithium metal anode (20–30 Å) [7]. This may produce entirely different reaction mechanisms on the surfaces on the lithium metal anode and the disordered carbon electrode. At present, the reaction mechanism on the disordered carbon electrode is not known in detail. We believe that other chemical or electrochemical reactions also occur simultaneously with solvent decomposition. Our FTIR results have shown that the composition of the SEI is very complex. There are some compounds which contain C–H bonds (bands at 2918 and 2846 cm^{-1}) and COOH groups (1660 cm^{-1}), and Li_2CO_3 (bands at 1528, 1437 and 867 cm^{-1}) on the surface of the discharged disordered carbon electrode [1]. From a comparison with the thickness of the SEI formed on the HOPG [6], it is obvious that the thickness of the SEI is larger than that formed on the HOPG. It can be postulated that the structure of the carbon electrode also influences the thickness of the SEI. It is known that the ICL produced on the disordered carbon electrode during the first cycle is larger than that on the graphite electrode.

Further experimental studies show that there is no significant change in the morphology of the disordered carbon electrode after several cycles. This finding is consistent with known results of electrochemical studies involving coulombic efficiency [1], in which the ICL is attributed to the intrinsic structure defect and the form of the SEI during the first cycle.

Although the SEI formed on the disordered carbon electrode can suppress further solvent decomposition, the increased thickness of the SEI will affect the diffusion rate of lithium ions during the charge and discharge processes. It is well-known that the rate of charge and discharge is very important for rechargeable batteries. Further work will focus on decreasing the thickness of the SEI on the surface of disordered carbon electrodes.

4. Conclusions

It is found that a SEI with a hill-like structure is formed on the surface of a disordered carbon electrode after the first cycle. The thickness of the SEI is in the range 60 to 200 nm. The SEI is much thicker than that formed on the surface of either a lithium metal anode or a graphite electrode.

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