Morphology Control of Lithium Deposited in Nonaqueous Media

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An artificial control of the morphology of lithium deposited in nonaqueous media was successfully accomplished by using the surface modification of the as-received lithium metal foil with HF treatment, to suppress the dendrite formation of lithium during the electrochemical deposition.

The artificial control of the morphology of deposits is in the question for the general chemistry. A lot of theoretical and experimental researches have been performed to clarify the relationship between the morphology and the deposition parameters.[1-4] On the other hand, the electrochemical deposition of alkali metal in nonaqueous media has been investigated by many researchers. However the artificial morphology control of lithium has never been reported in anywhere. Particularly, since the lithium metal has a high reactivity with water, oxygen, and nitrogen etc., the lithium surface is always covered with a native film. The lithium ions go through this film during the deposition and dissolution. In this regard, the surface state of lithium may influence strongly the morphology of lithium which is strongly related to the rechargeability of lithium anodes of rechargeable lithium batteries. Recently the surface analyses have been performed by several research groups using X-ray photoelectron spectroscopy (XPS), Fourier Transform Infrared Spectroscopy, and electrochemical methods.[5-8] We also made XPS analyses for lithium surfaces immersed in various electrolytes and proposed the new surface reaction mechanisms of the lithium metal anode.[9-13] In this study, the artificial surface modification for the lithium metal anode was accomplished by applying HF treatments.

The native surface film has been analyzed by XPS.[9] The outer part of the native film consists of Li_2CO_3 or LiOH and the inner one consists of Li_2O. The native film of lithium reacts with the electrolyte solution on its immersion, if a small amount of acids is contained in the electrolyte solution.[9, 10, 11] The chemical composition, structure, and stability of the surface film change according to the following equations, if propylene carbonate containing 1.0 mol dm^{-3} $LiPF_6$, for example, is used as the electrolyte solution in which a higher concentration of HF is contained than in other electrolytes.

$$LiOH+HF \rightarrow LiF+H_2O$$
$$Li_2O+2HF \rightarrow 2LiF+H_2O$$
$$Li_2CO_3+2HF \rightarrow 2LiF+H_2CO_3$$

When this electrolyte solution is used, a hemispherical lithium deposition has sometimes been observed, though the reproducibility was not high. It is desired to develop a useful means to artificially control the lithium surface conditions. In this study, attempts were made to treat the native film of lithium with HF in pure solvent to obtain a more reproducible lithium surface.

A lithium metal foil was put in propylene carbonate containing 5.0×10^{-4} mol dm^{-3} HF for 3 days. Fig. 1 shows XPS spectra of Li 1s for the lithium before and after the HF treatment. Before treatments, an intensity peak assigned to Li_2CO_3 or LiOH (55.0 eV) was shifted toward higher binding energy by 0.5 eV, suggesting that the native film was converted to LiF (56.0 eV). Correspondingly, the formation of LiF at the outer part of the surface film was observed from the XPS spectra of F 1s and the consumption of LiOH or Li_2CO_3 was confirmed from the XPS spectra of O 1s. The thickness of the surface film of the HF treated lithium was thin, as compared with the native film. The modified lithium was washed by pure propylene carbonate and then was transferred to the electrochemical cell. After several minutes, the electrochemical deposition of lithium on the modified surface was performed in propylene carbonate containing 1.0 mol dm^{-3} $LiPF_6$ at 0.2 mA cm^{-2} for 1 C cm^{-2}.

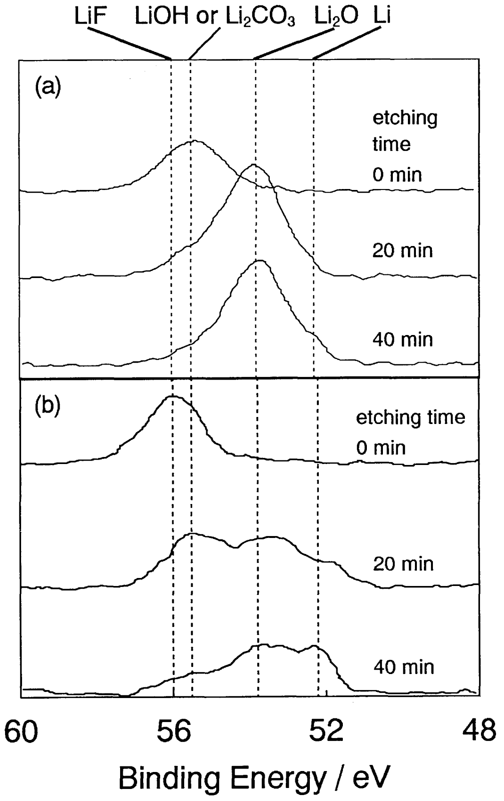

Figure 1. XPS spectra of lithium surface (a) before and (b) after the HF treatment, the HF treatment was peformed by the immerson of as-received lithium foil in propylene carbonate containing 5.0×10^{-4} mol dm^{-3} HF for 3 days, etching conditions : 2 kV and 7~8 μA (etching rate : 0.3~0.7 nm/min).

Figure 2 shows a scanning electron micrograph of lithium deposited on the modified lithium. The morphology of the deposited lithium was a hemispherical form. Any irregularity was not observed on the whole surface of the lithium metal, indicating that the surface treatment with HF is really useful to suppress the formation of lithium dendrites.

After the first discharge, the lithium surface was analyzed by XPS. The surface film formed by HF treatment remained on the

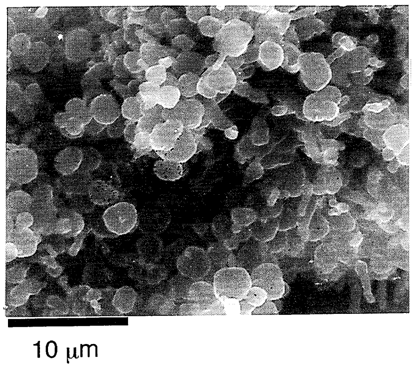

Figure 2. Scanning electron micrograph of lithium electrodeposited on the as-received lithium modified with the HF treatment, after the first electrochemical deposition.

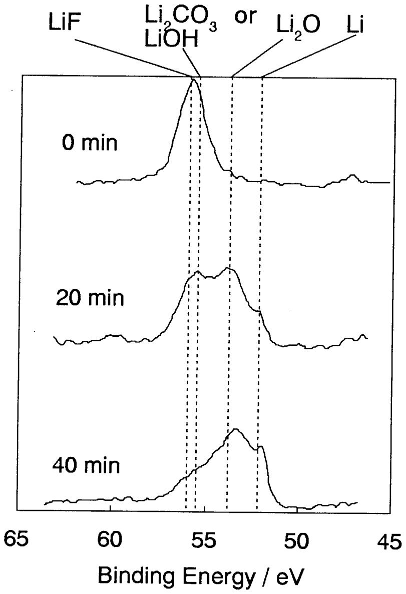

Figure 3. XPS spectra of Li 1s for lithium deposited on the as-received lithium which was modified by the HF treatment, obtained after 5 deposition and dissolution cycles, etching conditions : 2 kV and 7~8 μA (etching rate : 0.3~0.7 nm/min).

substrate.

Figure 3 shows XPS spectra of Li 1s for lithium deposited on the lithium surface modified with HF treatment, after 5 deposition and dissolution cycles. The spectra was very similar to those in Fig.1, evidencing the surface film of lithium treated with HF was sustained during the electrochemical deposition of lithium in propylene carbonate containing 1.0 mol dm^{-3} $LiPF_6$. Probably lithium ions go through this surface film during the electrochemical deposition to make deposition at the interface between lithium and its surface film. Even after five dissolution and deposition cycles, no dendrite was observed, as shown in Fig. 4.

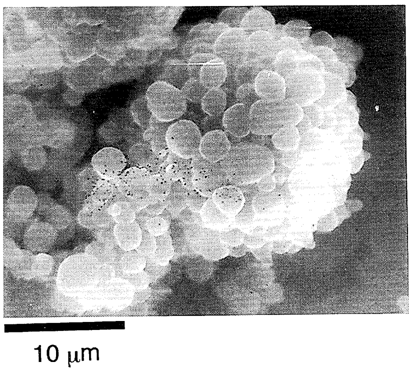

Figure 4. Scanning electron micrograph of lithium electrodeposited on the as-received lithium modified with the HF treatment obtained after five dissolution and deposition cycles. Deposition and dissolution currents : 0.2 mA cm^{-2} and the total deposition charge : 0.48 C cm^{-2}.

The current distribution is the most important factor in controlling the morphology of the deposited metal. If the surface film is not uniform, the current distribution can be localized to the specific points to give dendrite deposition. In contrast, the deposition of hemispherical form which could be obtained by a uniform current distribution on the lithium electrode. This fact suggests that the surface film obtained by HF treatment has a leveling effect for the current distribution. In conclusion, the surface modification using HF treatment is very effective for suppressing the dendrite formation of lithium.

References and Notes

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