Electrodeposition and electrochemical dissolution of Li metal onto an ultra-micro electrode

Kei Nishikawa[1], Chunyan Li[1] and Kiyoshi Kanamura[2]

[1] National Institute for Materials Science
1-1, Namiki, Tsukuba
Ibaraki 305-0044, Japan
Phone: +81-29-860-4387 E-mail: NISHIKAWA.Kei@nims.go.jp
[2] Tokyo Metropolitan University
1-1, Minami-Osawa, Hachioji,
Tokyo 192-0397, Japan

Abstract

Li metal is a promising anode material for Li batteries. In order to understand the mechanism of electrodeposition and electrochemical dissolution of Li metal, ultra-micro-electrode (UME) was utilized. UME technique can make it possible to do qualitative and quantitative analysis for morphological variation of electrodeposited Li metal. Furthermore, the cross-sectional observation was also conducted by FIB-SEM technique. It revealed the three-dimensional structure of the electrodeposited Li metal.

1. Introduction

Li metal is very attractive anode materials for next-generation Li batteries because of very large capacity density. The theoretical capacity is about 3800 mAh g^{-1}. It is ten times larger than that of current graphite anode of Li-ion batteries. However, Li metal shows large irreversible capacity when it is used as an anode. It is caused by very rough surface morphology of electrodeposited Li metal, and short circuit phenomenon will occurs by the dendrite growth of Li metal in the worst case. The safety issue prevents the commercialization of Li metal batteries. It is indispensable to control the surface morphology of Li anode during long cycle and restrict the dendrite growth of Li metal, in order to utilize Li metal anode in commercial batteries. From 1990s, many researches about Li metal electrode had been done, especially, surface chemistry of Li metal was investigated by X-ray photoelectron spectroscopy, Fourier transformed infrared spectroscopy and electrochemical impedance spectroscopy. Li metal surface is covered by solid electrolyte interphase (SEI) layer in electrolytes. Some chemical species in electrolytes reacts with Li metal and the decomposition products are accumulated on the Li metal surface as soon as Li metal contacts with the electrolytes. The characteristics of SEI layer will be related with the current distribution for the electrodeposition of Li metal. Actually, many kinds of additives have been suggested in order to control the morphological variation of the electrodeposited Li metal. However, the cycle performance was not good compared with the graphite electrode in the actual Li-ion batteries.

In this study, ultra-micro-electrode (UME) is used as the working electrode (substrate for Li electrodeposition). In case of Li metal electrodeposition, the distribution of electrochemically active sites make difficult to discuss the morphological variation quantitatively. For example, when we use a 2032 coin cell, the diameter of electrode is about 15 mm. In that case, the morphology of electrodeposited Li metal is varied depending on the place of the working electrode (e.g. edge or center). It is difficult to analyze the morphological variation of electrodeposited Li metal. Therefore, UME is very powerful technique for quantitative and qualitative analysis for morphology of the Li metal electrode. The effect of electrolytes, applied current density, and applied electricity to the electrodeposition and electrochemical dissolution of Li metal is discussed in this study in order to reveal the electrochemistry of Li metal.
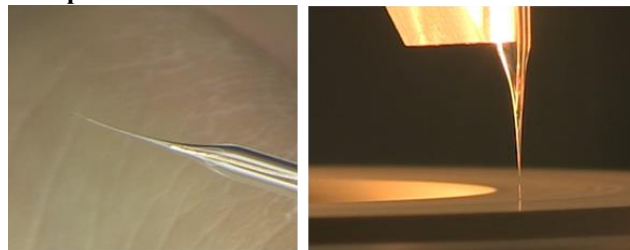
2. Experiments

Fig.1 Photos of UME. The Pt wire was inserted into glass capillary and the tip was polishes mechanically.

Fig. 1 shows the photos of ultra-micro-electrode (UME) used in this study. A Pt wire (10 μm diameter) was inserted into glass capillary and heat-sealed at the tip. And then, the tip was polished very carefully to obtain smooth surface. The Pt surface was coated by Cu electroplating because Li metal can form alloy phase with Pt. The UME was used as the working electrode for the electrodeposition and electrochemical dissolution of Li metal. The electrochemical cell was two-electrode cell, the counter electrode was Li metal. The electrolytes were varied. The Li salts were LiPF$_6$, LiClO$_4$, LiBF$_4$, LiTFSA, and LiFSA. The solvents were ethylene catbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC) and propylene carbonate (PC). Electrodeposition and electro-

chemical dissolution was conducted by an automatic potentiostat (SP-200, Biologic) under constant current condition. The experiments were done in super-dry room. The dewpoint of supplying air is below 183 K in the super dry room. After the electrochemical test, the tip of UME was put onto the airtight sample holder for SEM observation. The sample was transferred to SEM chamber without atmosphere exposure. The observation of surface morphology was conducted by FE-SEM (JSM-7800F, JEOL) and the cross sectional observation was conducted by FIB-SEM (SMF-200, Hitachi).

3. Results and Discussion

Fig.2 demonstrates the SEM images of electrodeposited Li metal with 2.0 mA cm^{-2} for 1hour (2 mAh cm^{-2}). The Li salt was LiPF$_6$ and the concentration was 1 mol dm^{-3}. The solvents were EC:DMC=1:1 mixed solvents, EC:PC=1:1 mixed solvents, EC, and PC.
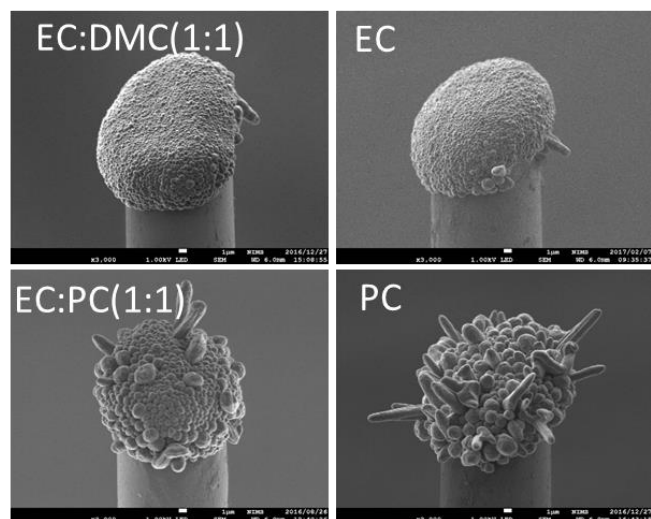

Fig.2 SEM images of the electrodeposited Li metal from 1.0 mol dm^{-3} LiPF$_6$ in various solvents.

When LiPF$_6$ was used as Li source in the electrolyte, the electrodeposited Li metal form rounded shape, but the smoothness was strongly dependent on solvent species. EC based solvents induces very smooth electrodeposited Li metal. Contrastingly, the PC solvent causes the rough and whisker-type Li metal. LiPF$_6$ based electrolyte includes HF because of the hydrolysis of LiPF$_6$ with H$_2$O as contaminant. HF induces LiF rich SEI layer on the electrodeposited Li metal. It is common feature for these electrolytes. However, the different solvents cause drastic difference of the morphology of the electrodeposited Li metal. It indicates that EC based solvents forms smooth and uniform SEI layer. PC will induces the less uniform SEI layer on the electrodeposited Li metal, and such SEI layer causes the non-uniform current distribution to form whisker-shape Li metal.

Fig.3 shows cross-sectional image obtained by cut and see technique with FIB-SEM system. The electrolyte was EC:DEC (1:1) containing 1 mol dm^{-3} LiPF$_6$. Applied current density was 2.0 mA cm^{-2}, and the duration was 1 hour (same condition of Fig.2). It shows that Li metal was electrodeposited with very dense column shape structure. Careful observation near substrate indicates that a lot of nucleation was occurred at the initial stage of the electrodeposition, and then the growth competition stage was appeared. Finally, the electrodeposition phenomenon got steady stable growth stage for very smooth surface. Such information must help to precise understand the mechanism of the electrodeposition of Li metal.
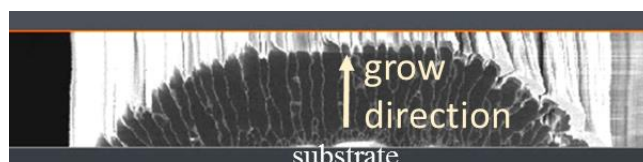

Fig.3 Cross sectional image of the electrodeposited Li metal from 1 mol dm^{-3} LiPF$_6$-EC:DEC=1:1 electrolyte.

4. Conclusions

Ultra-micro-electrode (UME) was utilized for the quantitative comparison of morphological variation of the electrodeposited Li metal. UME is very useful for SEM and FIB-SEM observation of the electrodeposited Li metal. Not only Li salts but also solvents species affect the morphology of the Li metal due to the variation of SEI layer on the Li metal. Cross sectional observation reveals the electrodeposited Li metal in 1 mol dm^{-3} LiPF$_6$-EC:DEC=1:1 electrolyte forms very dense and uniform column shape. This UME technique is very good model system for understanding the mechanism of electrodeposition and electrochemical dissolution of Li metal.

References
[1] K. Kanamura, S. Shiraishi, Z. Takehara, *J. Electrochem. Soc.* 143 (1996) 2187–2197.
[2] K. Nishikawa, T. Mori, T. Nishida, Y. Fukunaka, M. Rosso, T.Homma, *J. Electorchem. Soc.*, 157 (2010) A1212-A1217.