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Study on electrochemically deposited Mg metal

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ABSTRACT

An electrodeposition process of magnesium metal from Grignard reagent based electrolyte was studied by comparing with lithium. The electrodeposition of magnesium was performed at various current densities. The obtained magnesium deposits did not show dendritic morphologies while all the lithium deposits showed dendritic products. Two different crystal growth modes in the electrodeposition process of magnesium metal were confirmed by an observation using scanning electron micro scope (SEM) and a crystallographic analysis using X-ray diffraction (XRD). An electrochemical study of the deposition/dissolution process of the magnesium showed a remarkable dependency of the overpotential of magnesium deposition on the electrolyte concentration compared with lithium. This result suggests that the dependency of the overpotential on the electrolyte concentration prevent the locally concentrated current resulting to form very uniform deposits.

1. Introduction

Electrochemical energy storage devices are key components for innovative power train systems such as PHV, FCHV and EV. Especially for a long mile range EV, the energy density of the battery system is very critical. The battery system for the EV requires significantly higher energy density than that of state-of-art Li-ion battery. Therefore, finding new battery chemistry is very important as a future energy source for the EV [1].

For the high energy battery system, rechargeable lithium batteries using lithium metal have been studied for a long time, because of the high specific capacity of lithium metal; 2061 mAh cm^{-3} [2]. One of the major challenges for the lithium metal anode is the prevention of dendrite growth at the surface of the anode which has the possibility to lead a poor cycle performance and safety concerns [3]. Therefore, there has been extensive research on surface treatment, electrolyte additives, and solid state electrolytes to overcome this challenge [4,5].

We believe magnesium metal, which also has high specific capacity; 3833 mAh cm^{-3}, is another example of a potentially high capacity anode active material for the high energy battery system. To our knowledge, only a few research groups have studied to understand the electrochemical behavior of magnesium metal to confirm if it has the same issue of dendrite growth. Gregory et al. [6] have studied various kinds of Grignard reagent based electrolyte solutions and reported that the electro deposited magnesium obtained from organomagnesium chloride/$AlCl_3$ solution in THF showed dendritic morphology in a particular electrolyte composition.

Aurbach et al. have been studying deposition/dissolution mechanism of magnesium by using various analytical techniques; SEM, EQCM, *in situ* FTIR, *in situ* STM, NMR and so on [7–15]. Nakayama et al. [16] have characterized the electrochemical active species in the electrolyte solution by using NMR and Soft X-ray XAS. However among all of these papers, the dendrite formation process of electrodeposited magnesium has never been discussed. Furthermore there has been no systematic study to compare electrochemically deposited magnesium and lithium as anode active materials for a rechargeable battery system.

In the present study, electrodeposition of magnesium and lithium were performed and discussed how the deposition process affects to the morphology of deposits. Also the crystallographic study of the electrodeposited magnesium was conducted to discuss the crystal growth process of the magnesium during electrodeposition.

2. Experimental

In this study, all the electrochemical process of magnesium and lithium were performed by using a three electrode cell in a glove box filled with high purity argon. A polished platinum disc was used as the working electrode for the magnesium deposition and magnesium foil was used as the reference and the counter electrode. An electrolyte solution for magnesium deposition was prepared by mixing 1 ml of 2 M ethylmagnesium chloride in tetrahydrofuran (Sigma–Aldrich), 0.37 ml of dimethylaluminum chloride

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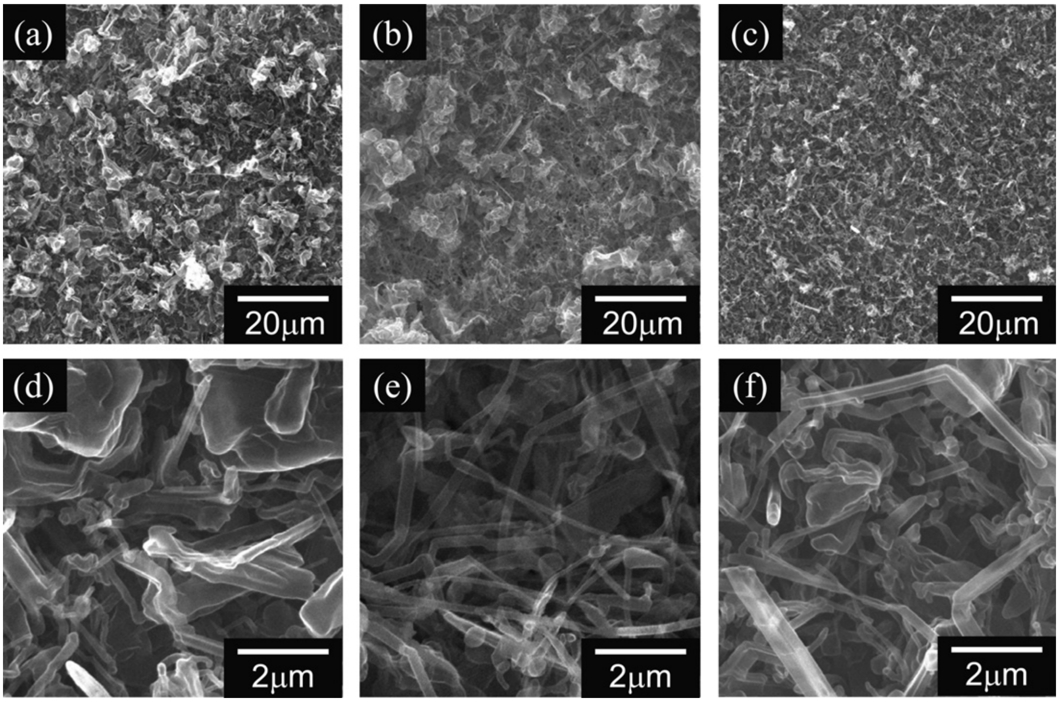

Fig. 1. SEM images of the electrodeposited lithium (a) 500×, 0.5 mA cm^{-2}, (b) 500×, 1.0 mA cm^{-2}, (c) 500×, 2.0 mA cm^{-2}, (d) 5000×, 0.5 mA cm^{-2}, (e) 5000×, 1.0 mA cm^{-2} and (f) 5000×, 2.0 mA cm^{-2}.

(Sigma–Aldrich) and anhydrous tetrahydrofuran (Sigma–Aldrich) [17]. The mixed solution was stirred for 24 h before the electrochemical measurements.

The electrodeposition of lithium was performed by using well polished nickel disc as a working electrode. Lithium foil was used as the reference and the counter electrode respectively. A conventional electrolyte solution; ethylene carbonate (EC) and diethyl carbonate (DEC) mixed solvent containing 1 M of lithium hexafluorophosphate ($LiPF_6$) purchased from Mitsubishi Chemical was used for the electrodeposition of lithium.

The electrodeposition of the magnesium and lithium was carried out by galvanostatic method under three different current densities; 0.5, 1.0 and 2.0 mA cm^{-2}. The electrodeposition processes were terminated by total electric charge at 1 C cm^{-2}. After the electrodeposition, the magnesium deposits were immediately rinsed with THF for 3 times to remove electrolyte solution and transferred to SEM by using special sample holder to avoid an exposure of the sample into air. In the case of the lithium, obtained specimens were rinsed with DEC instead of THF and transferred to SEM by following the same procedure as magnesium specimens.

The XRD analysis of the magnesium deposits were carried out with Cu-Kα beam (40 kV, 100 mA) at a scan rate 2° min^{-1} in the 2θ range 20–70°. In order to study the crystal orientation of the magnesium deposits, pole-figure measurement for (0 0 2) diffraction peak which appears 2θ at 34.447° was also performed for each deposit.

3. Result and discussion

SEM images of the lithium deposits are shown in Fig. 1. The lithium deposits obtained at 0.5 mA cm^{-2} and 1.0 mA cm^{-2} showed uneven surface morphology as shown in Fig. 1(a) and (b). Some whisker like lithium deposits (usually called just dendrite) were gathering to form porous deposition products as shown in magnified images (Fig. 1(d) and (e)). The lithium deposits obtained at 2.0 mA cm^{-2} are shown in Fig. 1(c). Although it shows relatively even surface morphology, it can be observed that the lithium deposit also consists of whisker like products as shown in the magnified image (Fig. 1(f)).

On the other hand, the magnesium deposits showed very different surface morphology compared with the lithium deposits as shown in Fig. 2. At first it can be said that all the magnesium deposits did not show a typical dendritic morphology in these three deposition conditions while all the lithium deposits showed dendritic and porous deposits. Fig. 2(a) and (b) shows the SEM images of the magnesium deposits obtained at 0.5 mA cm^{-2} and 1.0 mA cm^{-2} respectively. In both images, the magnesium deposits have round shaped grains with uniform size approximately 2–3 μm. The magnified images of these deposits showed that each grain has clear edge which is reflecting the hexagonal structure of magnesium. It indicates that the magnesium deposits have high crystallinity. The SEM images of the magnesium deposit obtained at 2.0 mA cm^{-2} are shown in Fig. 2(c). The magnesium deposit obtained at 2.0 mA cm^{-2} showed very different surface morphology from other two specimens. The specimen showed relatively small grains which are approximately had 0.5–1 μm resulting to form more smooth surface morphology and dense deposit comparing with other two deposits. The shape of each grain can be observed in the magnified images as shown in Fig. 2(f). The grains also had edges reflecting the crystal structure of magnesium however the observed grains had mainly triangle shape which suggests that the magnesium deposit obtained at 2.0 mA cm^{-2} could have different crystal orientation from other two specimens.

A crystallographic study for the magnesium deposits were performed by using XRD. Fig. 3 shows XRD patterns of the magnesium deposits. All the diffraction patterns showed peaks which is corresponding to magnesium or platinum which was used as substrate. According to the powder diffraction file PDF#04-003-2526, (0 0 2) diffraction which appears at 34.447° has 26.9% of the intensity of (1 0 1) diffraction at 36.630°. In the case of the magnesium deposits obtained at 0.5 mA cm^{-2} and 1.0 mA cm^{-2}, however, the intensity of (0 0 2) diffraction showed 81% and 77% of peak intensity compared with (1 0 1) diffraction respectively as shown in Fig. 3(a) and (b). Hence, it can be said that these magnesium deposits have (0 0 1)