ELECTROCEHMICAL STUDIES OF THE Mg_2Si THIN FILMS PREPARED WITH PULSED LASER DEPOSITION

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ABSTRACT

Electrochemically active thin films of Mg_2Si (film thickness of 137 nm) have been prepared with the pulsed laser deposition technique. The film showed stable cycle behavior at 0.1 ~ 1.0 V vs Li with capacity greater than 800 mAh/g for more than 100 cycles. Though film morphology become remarkably rougher with cycling, this film showed continuous high stability in cycling. The capacity retention might be attributed to limited structural volume change in 2-dimesional film, easier lithium diffusion to film surface and enhanced conductivity supported from stainless steel substrate. The goal of this film study is to help clarify capacity failure of powder intermetallics alloy anodes.

INTRODUCTION

The search for anode materials to replace graphite in rechargeable lithium batteries has intensified over recent years due to concerns about safety during overcharge in the presence of organic electrolyte and a highly oxidizing cathode material such as $LiCoO_2$.[1] Considerable effort has been devoted to find suitable alternative anodes among lithium binary[2] and intermetallics alloys[3-5] which operate a few hundred millivolts above metallic lithium. Magnesium silicide alloys have been studied for this application because Si has a good affinity for lithium.[6-8] Consensus regarding the electrochemical reaction between Li and Mg_2Si has not been reached. Part of the reason may be due to the fact that Mg_2Si is a semiconductor whose performance will be dependent on particle morphology and current density. However, porous electrodes from alloyed powders show rapid capacity fade over the first ten cycles. Much can be learned regarding the performance of low conductivity materials when they are in thin film form.[9] In addition, thin film electrodes comprise a “pure" material and simpler system; there is no complication from the amorphous carbon and binders which are necessary in powder-based porous electrodes. In the present work, we report our initial electrochemical studies of Mg_2Si thin film prepared on stainless steel substrate with the pulsed laser deposition (PLD) technique.

EXPERIMENTAL

Pure Mg_2Si films are prepared by PLD, at 250 ^oC and 100 mtorr Ar backpressure, onto polished (0.1 μm) 6 mm-diameter stainless steel substrates, sitting on a piece of silicon wafer. The target was pressed from Mg_2Si, which in turn was prepared by ball-milling Mg and Si metal powders. An XeCl eximer laser at 300 mJ/pulse at 10 Hz was used for PLD. The target-substrate distance was about 5 cm and the deposition time was 20 minutes. Prepared films appeared shiny and light blue colored. Film thickness was determined with field emission scanning electron microscope (Jeol 6340 FESEM). The Mg_2Si/Si film, left after removal of the Mg_2Si/SS substrate, was broken and a small film piece was tilted in the microscope to see the film cross section. The structure of the film was characterized by Raman spectroscopy. Raman spectra were recorded using a Labram Raman microscope, ISA Groupe Horiba at ambient conditions. All Raman spectra were recorded using the 632 nm line of a He-Ne laser at 1 mW. The size of the laser beam spot at the sample was > ~1 micrometer. Backscattering optics geometry with double notch filter and a standard CCD detector was used to collect, process and analyze the Raman signal. Films were studied electrochemically by embedding the 3 mm-thick disk into the end of a Kel-F rod which was inserted into a polypropylene cell fitted with lithium reference and counter electrode foils and filled with about 5 ml of 1M $LiPF_6$/EC/DMC (1:2) electrolyte (EM Industries).[9] Cyclic voltammetry (CV) with a sweep rate of 0.1 mV/s, and charge-discharge cycling at a constant current of 35 $\mu A/cm^2$ were used for film characterization. The surface images of Mg_2Si film before and after electrochemistry were obtained using atomic force microscope (AFM, Picoscan by Molecular Imaging), operating in contact mode with Si_3N_4 cantilever (cantilever force constant= 0.05 N/m).

RESULTS

Film Characterization

The film thickness measured by SEM cross section image was 137 nm but the film was not crystalline. No structure was discernable from the XRD of the film, therefore it was identified that this film is amorphous. Raman evaluation gave some film structural information, though an amorphous property was detected from ambiguous spectral feature of the film. Figure 1 shows Raman spectra of target, PLD film and Si wafer. Note that Mg_2Si has cubic structure with the lattice symmetry of *Fm3-m*, predicting A_{1g}, E_g, F_{2g} Raman active vibration modes.[10] Very strong F_{2g} and weak A_{1g} bands appear in the target but the E_g band is negligible in this material. Raman spectrum of film compared well with that of target except for a missing F_{2g} band. It has been reported that the F_{2g} band will predominate over the other bands when the laser focused on the (100) plane of a Mg_2Si single crystal but will become weaker or disappear on the (010) plane.[11] Based on this information, the missing F_{2g} band suggests that the film is oriented in the (010) plane. Additionally, it was found that the Mg_2Si PLD film had no isolated Si phase indicating pure Mg_2Si film formation by PLD.

Electrochemical Film Evaluation

The first lithium insertion into the film was done with slow-sweep CV as shown in Figure 2. Film overcharge efficiency was measured by integrating the anodic and cathodic portions. The first cycle showed 18.3 % overcharge followed by 14.2 and 11.2 % becoming more stable on cycling. There have been a few proposed reaction mechanisms between lithium and Mg_2Si.[6-8] Li-Mg alloying-dealloying occurs near 0.3 V, and Li-Si alloying-dealloying as well as lithiation-delithiation of Mg_2Si near 0.65 V, respectively. The positions of the CV peaks were quite consistent from the same run but a small cathodic peak at 0.2 V at the first cycle disappeared in the second and third cycles. This behavior seems to be associated with formation of solid electrolyte interface (SEI) layer on the electrode surface during cycling as it has been reported for graphite electrode.[12]

Galvanostatic plots were subsequently performed to observe any capacity loss with cycling. Figure 3 exhibits the results of 100 charge-discharge cycles at a current density of 35 $\mu A/cm^2$. Gravimetric capacity was calculated based on film thickness (137 nm), electrode area (0.283 cm^2) and the theoretical density (1.99 g/cm^3) of Mg_2Si. This film electrode underwent stabilization or increase in capacity greater than 800 mAh/g. The excellent cycling stability of this film electrode, compared to the rapid capacity fade reported for powder electrode, is noteworthy.

Self-discharge reaction is apparent for this film. When the film is in relaxation after charging to 0.1 V, potential tends to increase slowly to near 1.0 V. This behavior suggests that side reaction with the electrolyte may be responsible for the low coulombic efficiency shown in Fig. 3. The coulombic efficiency is even worse for cycling than for CV. However, increasing efficiency with cycle number suggests a slowing in the side-reaction with the build-up of the SEI layer. Examination of the chemistry of this layer is the subject of future work.

AFM was used to examine film morphology before and after electrochemical cycling. AFM surface images (Figure 4) represent small grains >50 nm cover a rough surface (76Å roughness) of stainless steel substrate, resulting in reduced roughness to 17 Å. However the surface morphology of the film has been substantially modified after cycling. The roughness of the film increased 24 times after electrochemistry (407 Å). Small grains are still observed in the film but most of them seemed to be agglomerated or coated by a SEI layer. Though the agglomeration was being made during lithiation-delithiation, it is amazing to see a continuous stable cycling as observed in the Figure 3.

It is generally observed that powder intermetallic alloys that undergo severe crystal structural changes during lattice volume expansion-contraction, also undergo particle morphology changes such as crumbling/cracking with cycling, causing capacity fade. The stable behavior observed with the thin film electrodes in this study, even in the presence of agglomeration with cycling, may be due to their amorphous character. In addition to the general geometrical (2-dimnesion) advantage of thin films, PLD films have a particularly strong physical adherence to substrate. This may inhibit volume change in the particles while its electrical conductivity is enhanced by substrate. It is possible that these factors tend to limit severe volume change and lead to faster lithium diffusion. The dependence of film behavior on thickness and the mechanisms of self-discharge will be examined in future work.

CONCLUSION

Thin PLD film of noncrystalline Mg_2Si showed a stable cycle behavior between 0.1 and 1.0V vs Li, serving a reversible capacity greater than 800 mAh/g. The better capacity retention in the film seems due to reduced lattice volume change and easier lithium diffusion in the film. Further electrochemical study on capacity failure of powder electrode should be undertaken for the Mg_2Si films with various film thickness.

ACKNOWLEDGMENTS

We would like to thank R. Reade for the preparation of the films, R. Kostecki for the AFM and Raman measurements and G. Roberts for Mg_2Si powders for target and helpful discussion. We are grateful to National Center for Electron Microscopy (NCEM) of Lawrence Berkeley National Laboratory for FESEM images. This work was supported by the Office of Energy Research, Basic Energy Sciences, Chemical Sciences Division of the Department of Energy under contract No. DE-ACO3-76SF00098.

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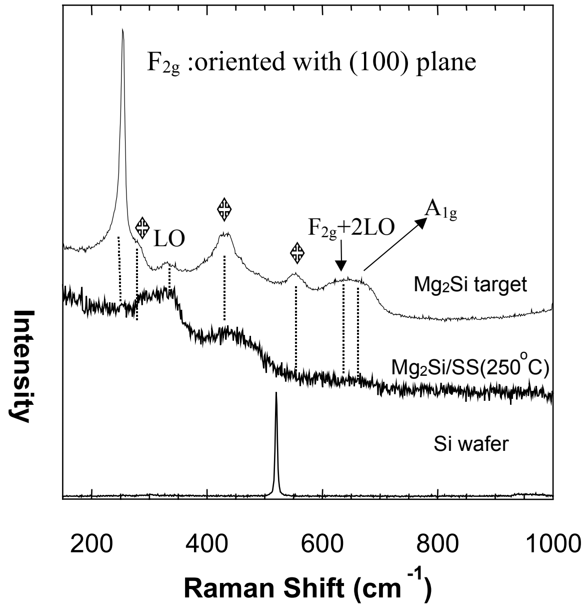

Figure 1. Micro-Raman spectra of Mg_2Si target, PLD film and Si wafer excited at 632 nm by He-Ne laser.

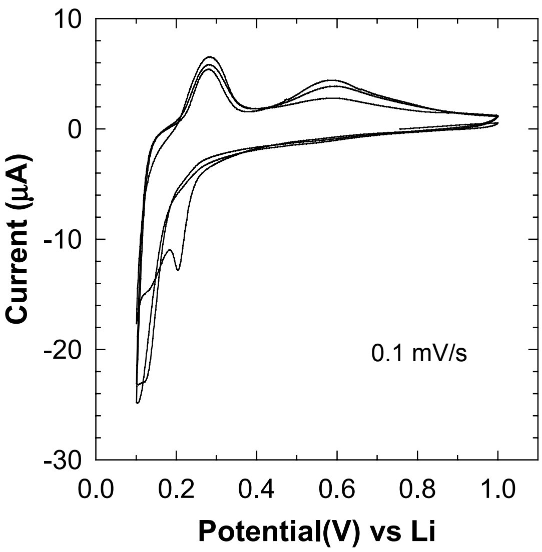

Figure 2. Cyclic voltammogram recorded for the Mg_2Si film.

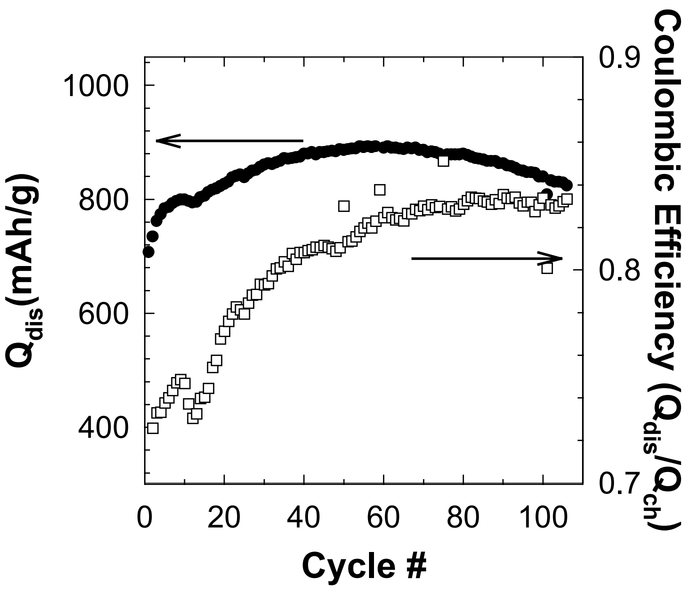

Figure 3. Plot of gravimetric capacity Q_{dis}(mAh/g) and coulombic efficiency (coulombs in discharge cycle/coulombs in charge cycle) vs cycle number for galvanostatic charge-discharge at 35 $\mu A/cm^2$ between 0.1 and 1.0 V in 1M $LiPF_6$-EC:DMC electrolyte.

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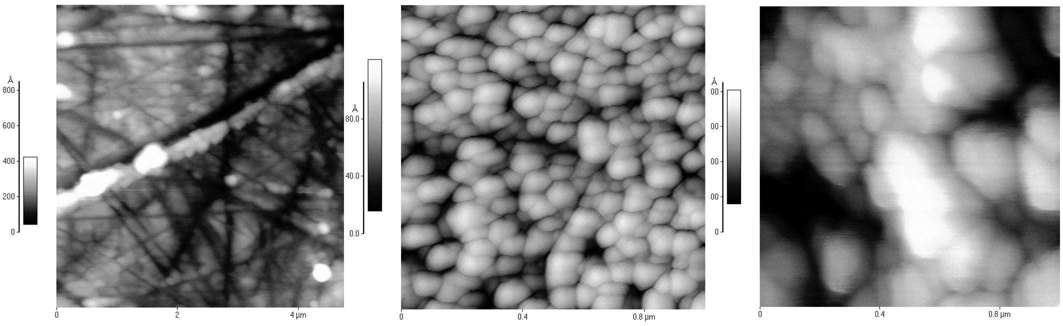
5μm×5μm | 1μm×1μm | 1μm×1μm



Stainless steel substrate | **As prepared Mg_2Si film** | **Film after EC**

Figure 4. Film surface morphology change observed by AFM before and after cycling.