

Electrochemical Studies of the Mg₂Si Thin Films Prepared with Pulsed Laser Deposition

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The search for anode materials to replace graphite in rechargeable lithium batteries has intensified over recent years. Metal silicide alloys have been studied for this application because of Si has a good affinity for lithium. Consensus regarding the electrochemical reaction between Li and Mg₂Si has not been reached^{1,2}. Part of the reason may be due to the fact that Mg₂Si is a semiconductor whose performance will be dependent on particle morphology and current density. Much can be learned regarding the performance of lower conductivity materials when they are in thin film form. In this work, we report our initial electrochemical studies of thin films of Mg₂Si prepared on stainless steel substrates with the pulsed laser deposition (PLD) technique.

The Mg₂Si films were prepared on stainless steel substrates with PLD at 250°C and 450°C in 10 mtorr of Ar. Deposition utilized a XeCl excimer laser at 10 Hz impinging on a target pressed from a ball-milled powder. Deposition times for the 250°C and 450°C films were 20 and 40 minutes, respectively. Films appeared shiny and are probably very thin, since no structure was discernable from XRD. However, Raman spectra of the films compared well with that of the target. In addition, the lower temperature film showed essentially none of the small amount of free Si phase present in the spectrum of the target and the higher temperature film.

For electrochemical measurements, films were mounted in a Kel-F holder and studied in a polypropylene cell with LiPF₆/EC/DMC electrolyte, and lithium foil counter and reference electrodes³. Films were cycled between voltage endpoints of 0.1 and 1.0 V vs. Li/Li⁺ at current densities of ± 17 and 35 μA/cm² for the low and high temperature films, respectively. The discharge capacity data for the two films is shown in Fig. 1. The film deposited at 450°C initially showed more than twice the capacity of the lower temperature film, probably reflecting a thicker film. However, the capacity of the low temperature film was much more stable over the 48 cycles tested.

Fig. 2 shows a differential capacity plot from the third cycle for the two films. Both films show charging at potentials below 0.25V, consistent with results from Kim et al.¹ The lower temperature film showed discharge plateaus (peaks in the DC plot) at voltages of 0.26 and 0.56 while that for the higher temperature films showed only the higher voltage peak. According to Kim, the higher voltage capacity may be due to the Li-Si alloy formation. This might be expected from the Raman spectra. Also shown in Fig.2 is a curve from the 40th cycle of the low temperature film. While the capacity has not changed significantly, the voltage profile shows the shift of some of the capacity from the lower to the higher voltage range.

Electrochemically active films of Mg₂Si have been prepared with PLD technique. Further analysis of film morphology before and after cycling as well the

performance of films prepared under different conditions and tested at various rates will be presented.

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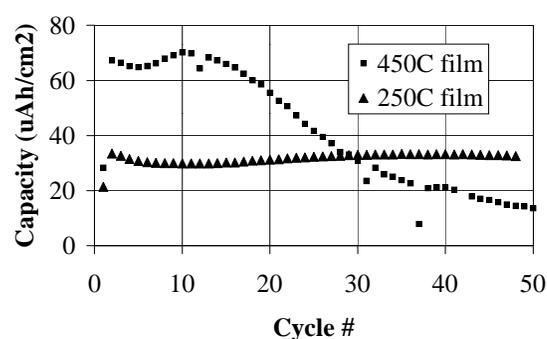


Figure 1. Cycling behavior for two Mg₂Si films in 1M LiPF₆/EC/DMC, at room temperature.

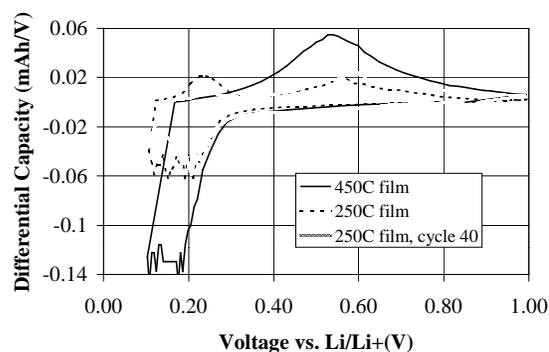


Figure 2 Differential capacity data for cycling of two Mg₂Si films (cycle 3 or 40) in 1M LiPF₆/EC/DMC, at room temperature.