

Thin-Film Cu₂Sb Electrodes Prepared by Pulsed Laser Deposition

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Intermetallics with the zinc blende type structure have recently been suggested as candidate alternative anode materials for replacing graphite in rechargeable lithium batteries.^{1,2} Cu₂Sb has available interstitial sites for lithium insertion. Fransson et al reported that lithium insertion into Cu₂Sb induced phase transformation to intermediate Li₂CuSb phase followed by an alloy reaction between Sb and Li.¹ Cu₂Sb is 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, thin films of Cu₂Sb electrode, prepared on stainless steel and copper substrates by pulsed laser deposition (PLD), have been used as a model system for the study of intermetallics electrochemical properties and reaction mechanism with lithium in the absence of carbon and binder materials.

The Cu₂Sb films were prepared on 3mm-thick stainless steel and copper foil (25 μ m) substrates with PLD at room temperature with 10 minutes deposition in 10 mtorr of Ar. Deposition utilized a XeCl excimer laser with energy density of 3-4 mJ/cm² at 10 Hz impinging on a target pressed from ball-milled powder. Films appeared shiny and light blue colored. The thickness of the film on stainless steel (SS), evaluated using FESEM, was 26 nm and major reflections of Cu₂Sb phase were discernable from XRD. The thickness of the film on Cu foil was estimated at 289 nm from deposition parameters.

Cu₂Sb/SS and Cu₂Sb/Cu films were cycled at constant current (35 μ A/cm²) at 0.1-1.2V and 0.0-1.2V vs. Li/Li⁺, respectively, in 1M LiPF₆/EC+DEC with Li foil CE and RE. For comparison with the PLD films, a laminate of Cu₂Sb powder electrode of 70% active Cu₂Sb, 20% carbon and 10% binder on Cu foil was also cycled (350 μ A/cm²) at 0.0-1.2V. The cell for the films on SS was described elsewhere.³ The films on copper and the powder laminate were cycled in Swagelok® cells with a RE and Celgard separator. The discharge capacities for the three types of electrode are shown in Fig. 1. The film on stainless steel initially showed large capacity followed by rapid capacity loss in ten cycles, while the capacity of the film on copper was more stable over the 50 cycles tested.

Fig. 2 shows differential capacity plots from the 1st and 25th cycles for the two films. Both films show charging at potentials 0.5-0.7V attributed to Li₂CuSb phase formation, consistent with previous results.¹ Both films showed discharge plateaus at voltages of around 0.9 and 1.0-1.1V. The higher voltage capacity may be due to the regeneration of Cu₂Sb phase. Also shown in Fig.2 is the disappearance of the charge and discharge peaks from the 25th cycle of the films. Structural lithium insertion is no longer occurring and all copper might be extruded. Nevertheless, the film on copper still shows a stable cycling (Fig.1) even

in the absence of those charge-discharge peaks. This is probably due to a reversible Li-Sb alloy reaction. It is suggested that extruded copper becomes stabilized on copper substrates and participates in supporting electronic conductivity of this material, while the copper on stainless steel may become locally isolated. Electrochemical crystallization observed by AFM images may be partly due to the isolation of copper, associated with a film degradation mechanism. Further electrochemical properties of films in window opening experiment as well as the performance comparison of films with that of powder electrode will be presented.

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References

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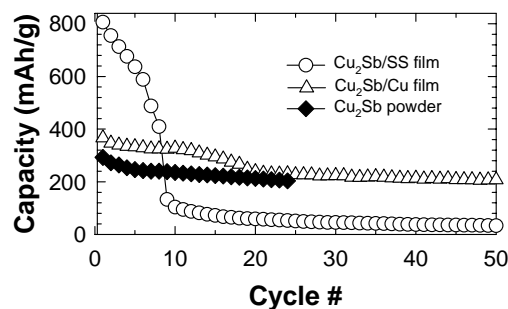


Fig.1. Cycling behavior for two Cu₂Sb films and powder electrode in 1M LiPF₆/EC+DEC, at room temperature.

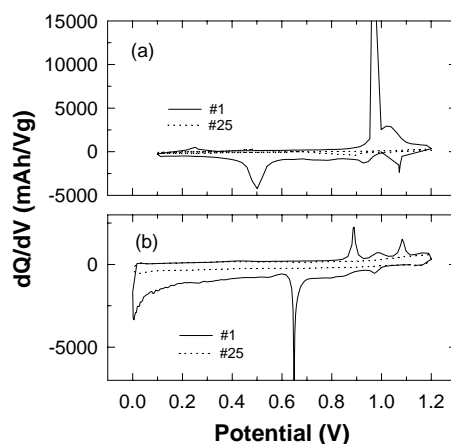


Fig. 2. Differential capacity data for cycling of (a) Cu₂Sb/SS and (b) Cu₂Sb/Cu films (cycle 1 or 25).