

# Progress in Vacuum Deposited Lithium Metal Anode Structures

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An industrial scale pilot machine for single sided vacuum coating of Lithium onto rolls of materials 340 mm wide was built some years ago and has coated Lithium onto many different substrates, from Polyolefin films to copper foils. To expand the design possibilities of metallic Lithium anodes, another, more complex machine has recently begun producing experimental and pilot materials. This new machine can coat Lithium onto polymer and foil webs of 150 mm width. In addition it can perform in-vacuum laminations and both single side and double side metallic Lithium coatings on selected substrates. It is used to perform feasibility studies and gather design data for production machines for economically viable combinations of materials. It is also involved in a NIST-ATP battery program. Scanning Electron Micrographs of the some of the Lithium surfaces produced will be discussed. Successful experiments depositing lithium layers from 2 to 40 microns thick onto various polymeric films have been performed. Thermo-physical conditions of gaseous lithium transfer from the vaporization source to the substrate were investigated. Design criteria for the Lithium vapor generator with minimum heat transfer are discussed.

### I. INTRODUCTION

As we have reported in previous work<sup>1</sup>, Sidrabe has extensive experience with depositing thick metal layers onto relatively thin polymeric films. Using a thermo-stabilization system with a proprietary, enhanced cooling system in the deposition zone, we have produced micron thick coatings of metals (Cu, Al, Ag, Ni) and of various alloys (stainless steel, Nichrome, Monel metal, etc.) on polymers. Coatings were produced at industrial speeds and coating thicknesses of up to 2 ... 5 microns.

Recently interest was expressed in the deposition of active metals, including lithium, for battery anode production. Users' requirements are for production of thick layers of lithium (3-30 microns) on very thin polymeric films, foils and combined metal and plastic materials. The effects of Lithium heat of deposition on the substrate during deposition were investigated.

The heat, transferred by lithium condensation on substrate during resistive evaporation consists of two parts:  $Q_k$  - heat transfer with deposited metal and  $Q_l$  - heat transfer by radiation from the heated evaporation device surfaces.

To achieve a design of a vapor generator with the desired low radiation transfer the relation between heat transfer to the web and source melt surface temperature was investigated.

Let us define the specific heat flow, transferred on substrate as:

$H_{tr}$  - specific heat transfer

$$H_{tr} = (Q_k + Q_l) / m \quad [\text{kJ/g}], \quad (1)$$

where  $m$  is the weight of deposited metal.

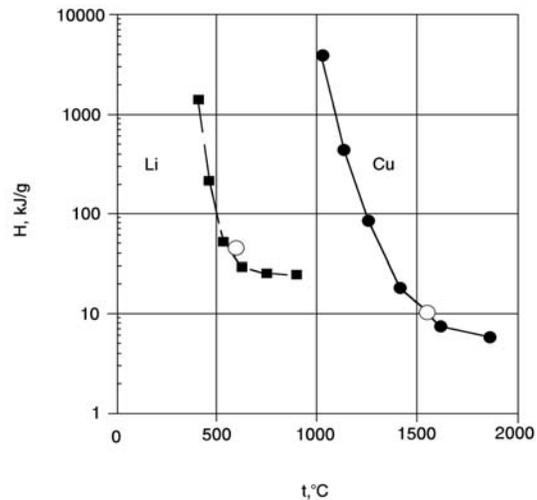


Figure 1 Li and Cu heat transfer at various evaporation temperatures.

Figure 1 shows the relationship between heat transfer value and melted metal surface temperature for lithium and copper. The  $H_{tr}$  value essentially depends on the evaporation temperature and the heat transfer decreases to certain optimal values as the temperature increases. At further temperature increases in evaporant temperature an insignificant growth of  $H_{tr}$  is theoretically expected, but this would be beyond the practical application zone.

Lithium heat transfer at the specific working points, indicated on the chart, is almost 5 times greater than the copper heat transfer. Taking into account densities of the two metals it might be shown that for

the deposition of 25 microns of lithium, the thermal load on the film is equal to that of depositing approximately 5 microns of copper. Despite the experience available, removal of such an amount of heat is a complicated task. Methods of heat removal in such systems have been studied for many years in several other metal systems and proprietary systems and processes have been developed. Providing constant evaporation speed over long process time is very essential during deposition of significant lithium amounts. From the heat transfer point of view the optimal system is a system of crucibles with the lithium melted like a mirror, distributed among several crucibles with minimum evaporation area in each, and uniformly covering the maximum deposition zone. Recently an excellent paper on the theory and results of Lithium evaporation from a single, simple crucible was published<sup>2</sup>. The additional supply of liquid lithium to all crucibles must go through a filtering system. It is also desirable to run returning liquid lithium from the crucibles through filters. In addition, at the end of processing a roll of material it is very desirable to remove the hot, liquid Lithium from the machine for the purpose of safety and more rapid cooling.

## II. EXPERIMENT

Preliminary research was carried out in a bell jar-type machine, providing deposition onto samples, 100 x 100 mm. Film samples were fixed onto a sector that imitates part of the thermostating drum surface and proprietary cooling process. Evaporation was from an open crucible with indirect melt heating up to a preset temperature. Up to eight samples were consecutively coated with lithium during one pumpdown cycle. The machine was provided with glove feedthroughs, placed behind gate valves during the cycle. A device for cutting samples, inserting them into shipping bags, and welding the bags was inside the vacuum volume.

The optimal deposition modes and the best underlayers between polymer film and lithium coatings were determined according to the research results. Theoretically determined relations between lithium heat transfer and temperature were verified and necessary factors of the heat transfer in the film-cooling surface system at equilibrium process were estimated. The heat transfer factor depends on many parameters including roughness of cooled surface, web-tensioning forces, chamber pressure value, etc. In the development system the heat transfer factor value is estimated in range 150 - 200 W/m<sup>2</sup> °C.

On the basis of theoretical and experimental results from the bell jar, a pilot roll-to-roll vacuum machine to

produce rolls of polymeric film or metal foils with lithium layers 2 ... 40 microns thick was built. The base material width is 340 mm. A masking system for formation of uncoated longitudinal stripes is also provided for short experimental runs.



Figure 2 Bell Jar for Lithium evaporation

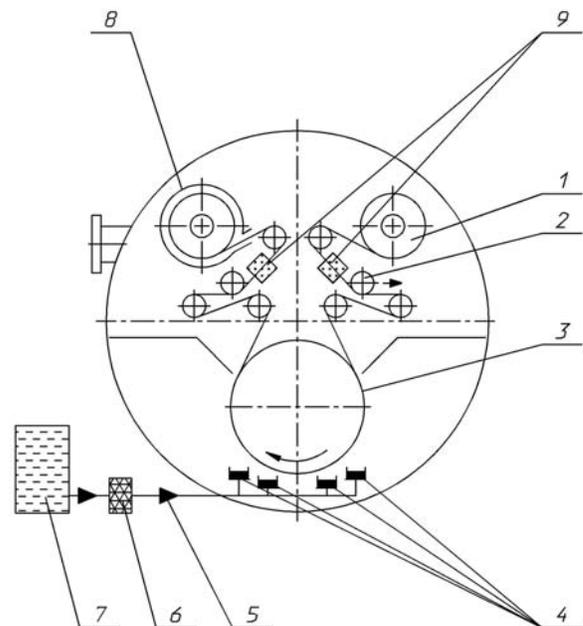


Figure 3 Layout of the lithium deposition machine

Figure 3 shows a simplified pilot vacuum machine layout. Figures 4, 5 show pictures of the pilot machine and winding device. The vacuum volume is divided into winding and deposition compartments. From unwinding roller (1) film is transported on spreader roller (2) and pressed to thermostat drum (3). The drum is cooled to low temperatures. In the deposition zone there is a system of crucibles (4), which are additionally fed with liquid lithium in hot transfer pipes (5) through filters (6) from a vessel (7) containing molten metal. Lithium coated film is wound through the system of rollers to the rewind roll, which is enclosed by a special transfer canister (8). When the coating cycle is finished and before dry air is admitted into the chamber, the canister is sealed and argon is supplied inside the canister up to the atmosphere pressure.



Figure 4 Vacuum pilot lithium deposition machine.

Measurement of the lithium layer thickness is made with radioisotopic sensors (9) using Beta-ray absorption techniques. A measurement for density estimation of base film and underlayers, deposited in another machine, is performed just before the lithium deposition.

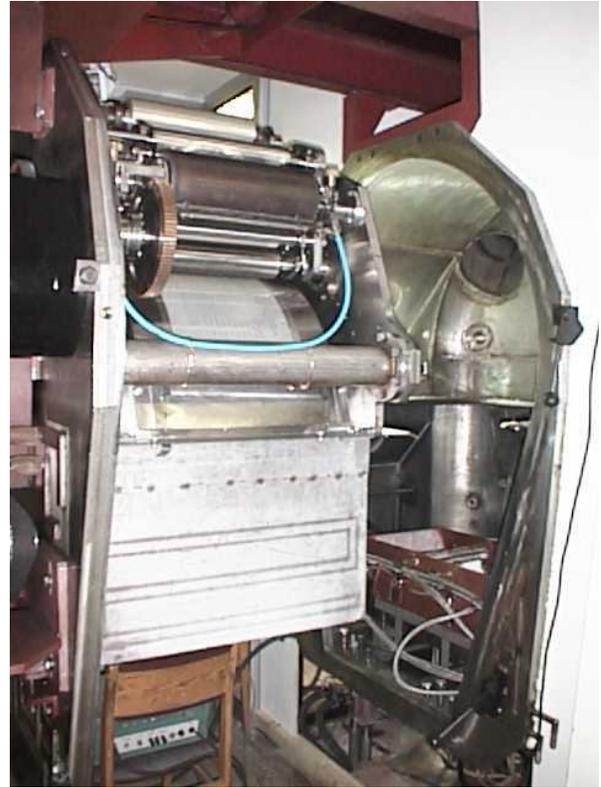


Figure 5 Winding device of the lithium machine



Figure 6 Lithium evaporation device.

Total density of combined layers is measured after the deposition zone. After computer processing of both signals, the thickness value of currently deposited lithium layer is displayed on the screen.

Figure 6 shows a lithium evaporation device and Figure 7 shows material with lithium deposited during winding using the masking device to stripe the deposit.



Figure 7 Lithium coated film during winding

At present we produce pilot lots of material on base webs of PET film 6 microns thick or more, coated with lithium in preset thickness range.

The new experimental narrow web coating machine for Li deposition onto roll substrates has greatly expanded our possibilities of creating unique lithium metal anode structures. It now allows us to manufacture materials with double-sided Li coating with one winding run of the substrate.

A simplified layout of the machine is shown in Fig. 8.

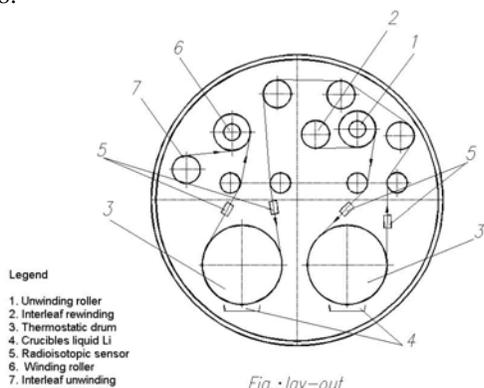


Figure 8 Schematic of new experimental Li coater.

The substrate arrives from the unwinding roller (1) to the first of two drums (3), where the first Li layer is deposited from the crucibles (4). As in the first machine, both processor drums are thermostatically controlled using advanced heat removal technology. If the substrate has an interleaf film, there is a wind-up roller (2) in the machine to rewind the interleaf. Further the material goes along the system of rollers to the second drum, where Li is deposited from the crucibles (4) onto the second side of the substrate. The product rewinding onto the roller (6) can be performed both with interleaf, e.g. OPP film (from the roller (7)), or without it. Deposition of one-side coating is also

possible on the machine. To accomplish this either of the two Li evaporators is not switched on. The machine is equipped with isotope detectors for Li thickness (5) and controlled with a PC. A partial view of the machine's inside arrangement is shown in Fig. 9.



Figure 9 View through port of web in Li coater

A sample of copper foil with double-side Li coating is presented in Fig 10.



Figure 10 Double side coated Li on Cu foil.

During check-out of the equipment and technology the following parameters on the a web of copper foil 10 microns thick have been achieved: For one-side coating deposition the Li thickness has been approaching 25 microns; For double-side coating Li thickness up to 20 microns for each side of the foil.

The surface properties of the deposited Li can vary a great deal. The microstructure of the surface will depend strongly on the structure of the base foil if foil is used. The second and equally strong influence is deposition rate coupled with web temperature. When depositing onto Polyolefin webs a very narrow range of these parameters is permitted. When depositing onto metal foils a much wider range is possible.

Figures 11 to 14 show some of the surface features seen.

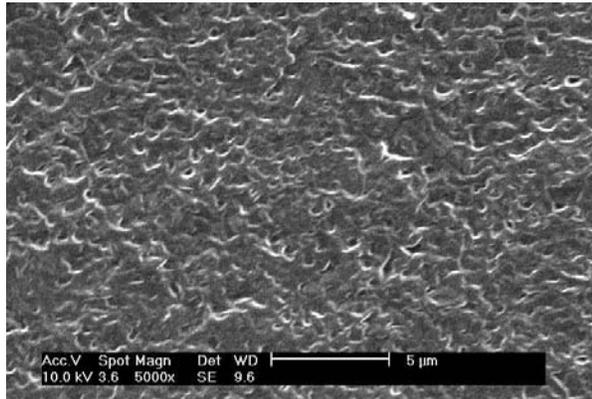


Figure 11 SEM of 12 microns of Li on metal coated PET, 5000x

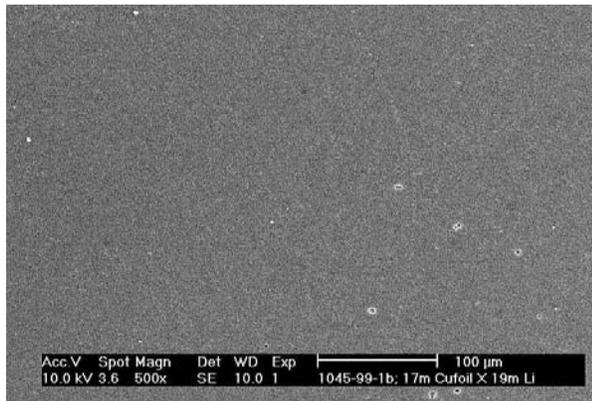


Figure 12 SEM of 19 microns of Li on 17 micron Cu foil, 500x

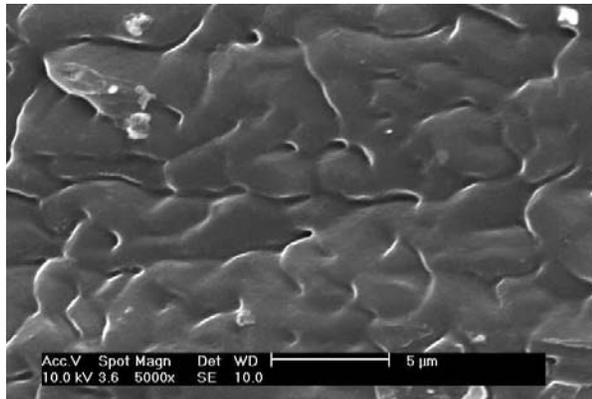


Figure 13 SEM of same material as Fig 12, at 5000x

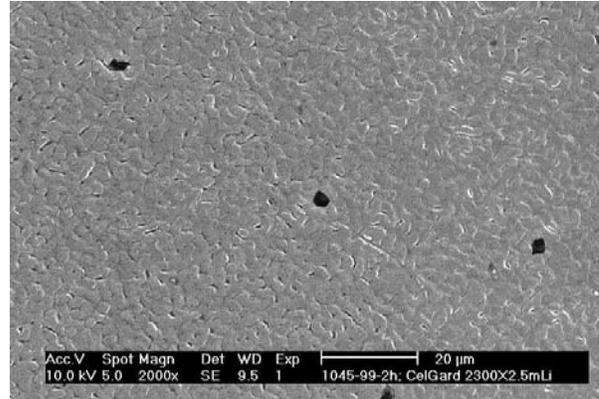


Figure 14 SEM of 2.5 microns of Li on Celgard material

### III. CONCLUSION

Theoretical and experimental aspects of process creation for deposition of thick lithium layers onto thin polymer films and foils have been investigated. The feasibility of lithium deposition up to 40 microns thick onto thin webs has been proven experimentally. Two prototype roll-to-roll machines have been built and are producing Li coated materials. The achieved results give a satisfactory basis for development of high-capacity industrial equipment.

### ACKNOWLEDGMENTS

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