



## Materials

### Polymer-Based Composite Catholytes for Li Thin-Film Cells

It should be possible to increase charge capacities and cycle lives.

NASA's Jet Propulsion Laboratory, Pasadena, California

Polymer-based composite catholyte structures have been investigated in a continuing effort to increase the charge/discharge capacities of solid-state lithium thin-film electrochemical cells. A cell according to this concept contains the following layers (see figure):

- An anode current-collecting layer, typically made of Cu;
- An Li metal anode layer;
- A solid electrolyte layer of  $\text{Li}_{3.3}\text{PO}_{3.8}\text{N}_{0.22}$  ("LiPON") about 1 to 2  $\mu\text{m}$  thick;
- The aforementioned composite catholyte layer, typically about 100  $\mu\text{m}$  thick, consisting of electronically conductive nanoparticles in an Li-ion-conductive polymer matrix; and
- A metallic cathode current collector, typically made of Mo and about 0.5  $\mu\text{m}$  thick.

In the fabrication of such a cell, the anode current collector (or, alternatively, the Li anode layer if already present as explained in the next paragraph) is first used as a substrate, onto which the

$\text{Li}_{3.3}\text{PO}_{3.8}\text{N}_{0.22}$  layer is deposited. The composite catholyte layer is then cast onto the  $\text{Li}_{3.3}\text{PO}_{3.8}\text{N}_{0.22}$  layer. Next, the cathode current collector is deposited on, or pressed into contact with, the composite catholyte layer.

If the anode current collector is a Cu film on a flexible substrate (as in prototype cells) or if it is something similar, the Li anode layer can be formed by plating of Li on the anode current collector during the first charge. Alternatively, the anode layer can be made, at the outset, of a thin film of Li; if this were done, the cell could retain a greater fraction of its capacity over many cycles because the film could be made to contain a slight excess of Li that would be available to replace some Li that is lost to the surroundings during cycling.

Inasmuch as  $\text{Li}_{3.3}\text{PO}_{3.8}\text{N}_{0.22}$  is an amorphous, flexible material, the cell as a whole can be a free-standing, flexible structure. Theoretically, the capacity of the cell can

equal or perhaps exceed that of a typical state-of-the-art lithium thin-film cell. The inclusion of the  $\text{Li}_{3.3}\text{PO}_{3.8}\text{N}_{0.22}$  is expected to result in extended lifetime and enables the use of Li in metallic form because the hazards associated with the combination of metallic Li and liquid electrolyte are not present. Further, it is anticipated that the cell would have long (relative to prior Li thin-film cells) cycle life at temperature up to 150 °C, provided that the proper cathode material is selected.

The capacities of the prototype cells thus far have been below theoretically attainable values. It seems likely that the theoretical values could be approached by selecting the proper cathode material and including thin Li anode films at the outset.

*This work was done by Jay Whitacre, William West, Keith Chin, and Sekharipuram Narayanan of Caltech for NASA's Jet Propulsion Laboratory. Further information is contained in a TSP (see page 1).*

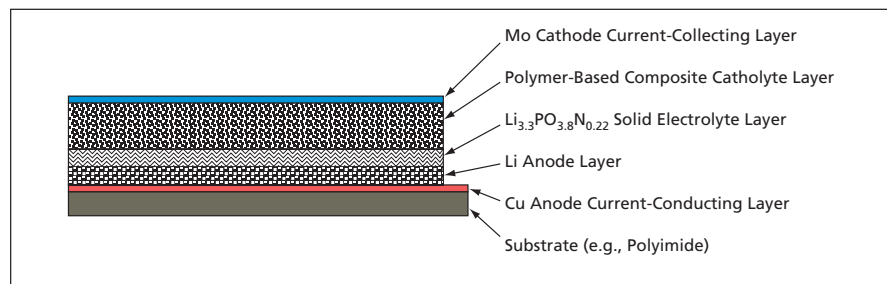
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A Polymer-Based Composite Catholyte Layer may be the key to high charge/discharge capacity in an Li thin-film cell. In prototype cells, the catholyte layers consisted of  $\text{LiCoO}_2$ , polyethylene oxide, lithium trifluoromethanesulfonate, and carbon black.

### Using ALD To Bond CNTs to Substrates and Matrices

CNT-based field emitters could be made more durable.

NASA's Jet Propulsion Laboratory, Pasadena, California

Atomic-layer deposition (ALD) has been shown to be effective as a means of coating carbon nanotubes (CNTs) with layers of  $\text{Al}_2\text{O}_3$  that form strong bonds between the CNTs and the substrates on which the CNTs are grown. It should also be possible to form strong

CNT/substrate bonds using other coating materials that are amenable to ALD — for example,  $\text{HfO}_2$ , Ti, or Ta. Further, it has been conjectured that bonds between CNTs and matrices in CNT/matrix composite materials could be strengthened by ALD of suitable coat-

ing materials on the CNTs.

The need to increase adhesion between CNTs and substrates on which they are grown was noticed in examination of prototype advanced field emitters consisting of arrays of vertically aligned bundles of CNTs grown on iron