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 Li_{3.3}PO_{3.8}N_{0.22} (“LiPON”) about 1 to 2 µm thick;
- The aforementioned composite catholyte layer, typically about 100 µm 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 µm 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 Li_{3.3}PO_{3.8}N_{0.22} layer is deposited. The composite catholyte layer is then cast onto the Li_{3.3}PO_{3.8}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 Li_{3.3}PO_{3.8}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 be strengthened by ALD of suitable coating 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 substrates consisting of arrays of vertically aligned bundles of CNTs grown on iron substrates.

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 Al_{2}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, 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 coating materials on the CNTs.
catalyst dots on silicon substrates. It was found that the CNTs are easily peeled off the substrates by abrasion or by pulling with adhesive tape and that the CNTs might also be pulled off the substrates by application of strong electric fields.

ALD is a previously developed vapor-phase thin-film-growth technique. The full name of the technique reflects the fact that it is possible to tailor the film thickness to a precision of the order of a single layer of deposited atoms and, thus, to form a highly uniform, conformal coating. ALD differs from conventional chemical vapor deposition, in which material is deposited continually by thermal decomposition of a precursor gas. In ALD, material is deposited one layer of atoms at a time because the deposition process is self-limiting and driven by chemical reactions between the precursor gas and the surface of the substrate or the previously deposited layer. In order to enable growth of the next layer, it is necessary to first effect an activation subprocess that imparts the needed chemical reactivity to the surface. Thus, the thickness of the deposit can be tailored by simply choosing the number of activation/growth cycles.

The use of ALD for coating CNTs to increase adhesion was demonstrated in experiments on specimens comprising multivalled CNTs grown to lengths of hundreds of microns extending away from 2.5-nm-thick iron catalyst layers on silicon substrates. The CNTs were coated with Al2O3 by ALD using trimethoxyaluminum and water vapor as precursor gases at a growth temperature of 250 °C. The Al2O3 was deposited to a thickness of 170 nm in 1,700 activation/growth cycles. Preparation of the specimen surfaces prior to ALD was found to be necessary for the success of the ALD: Specifically, it was found to be necessary to heat the specimens in air at a temperature of 500 °C to increase the density of hydroxyl groups on the substrate and CNT surfaces that enable formation of covalent bonds with the Al2O3 deposits. In the absence of such preparation, the Al2O3 deposits separated from the substrate surfaces.

The adhesion strengths of the ALD-coated CNTs were quantified by pull tests using known weights. For example, in the case of one specimen containing an array comprising 5-µm-diameter bundles of CNTs separated by 5-µm gaps, the measured adhesion strength was 1.25 MPa. It should be noted that this measurement sets a lower bound inasmuch as the strength value was calculated by dividing the applied force by the specimen area. After accounting for the fact that the entire specimen area was not covered by CNTs, the adhesion strength was estimated to be >10 MPa.

This work was done by Eric W. Wong, Michael J. Bronikowski, and Robert S. Kowalczyk of Caltech for NASA’s Jet Propulsion Laboratory.

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# Alternating-Composition Layered Ceramic Barrier Coatings

These coatings are expected to be more durable, relative to prior thermal/environmental barrier coatings.

*John H. Glenn Research Center, Cleveland, Ohio*

Ceramic thermal and environmental barrier coatings (T/EBCs) that contain multiple layers of alternating chemical composition have been developed as improved means of protecting underlying components of gas-turbine and other heat engines against both corrosive combustion gases and high temperatures. A coating of this type (see figure) is configured using the following layers:

- An outer, or top oxide layer that has a relatively high coefficient of thermal expansion (CTE) and serves primarily to thermally protect the underlying coating layers and the low-CTE ceramic substrate structural material (the component that is ultimately meant to be protected) from damage due to exposure at the high temperatures to be experienced in the application;

- An inner, or bottom silicon-containing/silicate layer, which is in contact with the substrate, has a low CTE and

Alternating-Composition Intermediate Layers dissipate strain energy arising from the thermal-expansion mismatch between the inner and outer coating layers.