# Materials

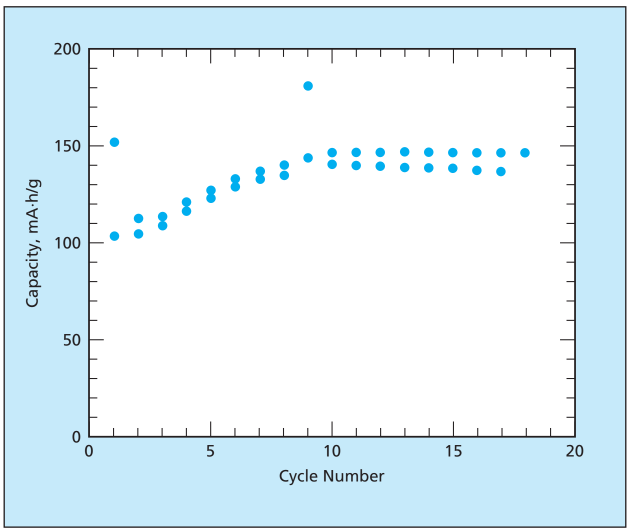
## Nanostructured $MnO_2$-Based Cathodes for Li-Ion/Polymer Cells

**Experiments show promise for increasing energy densities.**

*Lyndon B. Johnson Space Center, Houston, Texas*

Nanostructured $MnO_2$-based cathodes for Li-ion/polymer electrochemical cells have been investigated in a continuing effort to develop safe, high-energy-density, reliable, low-toxicity, rechargeable batteries for a variety of applications in NASA programs and in mass-produced commercial electronic equipment. Whereas the energy densities of state-of-the-art lithium-ion/polymer batteries range from 150 to 175 W·h/kg, the goal of this effort is to increase the typical energy density to about 250 W·h/kg. It is also expected that an incidental benefit of this effort will be increases in power densities because the distances over which Li ions must diffuse through nanostructured cathode materials are smaller than those through solid bulk cathode materials.

The developmental $MnO_2$-based cathode nanostructures are, more specifically, layered structures that have compositions of $Li_xMn_{1-y}M_yO_2$ (where $x \geq 0$, $0 \leq y \leq 1$, and M denotes a dopant metal other than Mn or Li). The average size of crystallites in cathodes made from nanolayered $Li_xMn_{1-y}M_yO_2$ was observed to be about 50 nm. The energy densities of these cathodes were found to be approximately 440 W·h/kg. The charge/discharge curves of these cathodes were observed to lie in the potential range of 4.2 to 2 V and to be continuous. The nanostructures were found to be stable and the charge/discharge capacities of the cathodes were found not to fade after multiple charge/discharge cycles (see figure).




The **Charge/Discharge Capacities** of $Li_xMn_{1-y}M_yO_2$ cathode materials were observed not to decrease below initial values after 20 charge/discharge cycles.

The experiments performed thus far have involved small laboratory cells. Further research will be needed to demonstrate practical cells. The tailoring of nanostructures and compositions is likely to be an important topic of research because the electrochemical properties of $Li_xMn_{1-y}M_yO_2$ from which the cathodes are made depend on the sizes of the crystallites, and the type and the amounts of dopants.

*This work was done by Ganesh Skandan and Amit Singhal of Nanopowder Enterprises Inc. for* **Johnson Space Center**.

*In accordance with Public Law 96-517, the contractor has elected to retain title to this invention. Inquiries concerning rights for its commercial use should be addressed to:*

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*Refer to MSC-23368, volume and number of this* NASA Tech Briefs *issue, and the page number.*

## Multi-Layer Laminated Thin Films for Inflatable Structures

**Laminates offer advantages over equal-thickness monolayer sheets.**

*NASA's Jet Propulsion Laboratory, Pasadena, California*

Special-purpose balloons and other inflatable structures would be constructed as flexible laminates of multiple thin polymeric films interspersed with layers of adhesive, according to a proposal. In the original intended application, the laminate would serve as the envelope of the Titan Aerobot — a proposed robotic airship for exploring Titan (one of the moons of Saturn). Potential terrestrial applications for such flexible laminates could include blimps and sails.

In the original application, the multi-layered laminate would contain six layers of 0.14-mil (0.0036-mm)-thick Mylar®, (or equivalent) polyethylene terephthalate film with a layer of adhesive between each layer of Mylar®. The overall thickness and areal density of this laminate would be nearly the same as those of 1-mil (0.0254-mm)-thick monolayer polyethylene terephthalate sheet. However, the laminate would offer several advantages over the monolayer sheet, especially with respect to interrelated considerations of flexing properties, formation of pinholes, and difficulty or ease of handling, as discussed next.

Most of the damage during flexing of the laminate would be localized in the outermost layers, where the radii of bending in a given bend would be the largest and, hence, the bending stress would be the greatest. The adverse effects of formation of pinholes would be nearly completely mitigated in the laminate because a pinhole in a given layer

A **Flex Testing Apparatus** repeatedly twists and compresses a sample of material.

would not propagate to adjacent layers. Hence, the laminate would tend to remain effective as a barrier to retain gas. Similar arguments can be made regarding cracks: While a crack could form as a result of stress or a defect in the film material, a crack would not propagate into adjacent layers, and the adjacent layer(s) would even arrest propagation of the crack.

In the case of the monolayer sheet, surface damage (scratches, dents, permanent folds, pinholes, and the like) caused by handling would constitute or give rise to defects that could propagate through the thickness as cracks or pinholes that would render the sheet less effective or ineffective as a barrier. In contrast, because damage incurred during handling of the laminate would ordinarily be limited to the outermost layers, the barrier properties of the laminate would be less likely to be adversely affected. Therefore, handling of the laminate would be easier because there would be less of a need to exercise care to ensure against surface damage.

For the Titan Aerobot, the laminate is required to retain its physical properties (especially flexibility and effectiveness as a barrier) to a sufficient degree at temperatures as low as that of liquid nitrogen. To evaluate this laminate and other candidate materials, a flex testing apparatus (see figure) has been used to repeatedly flex samples of the materials with a 45° twist and a 2-in. (≈5-cm) compression while the samples were immersed in liquid nitrogen. After having been flexed a set number of cycles, samples were examined by use of an apparatus that can easily detect gas leaks from through pinholes as narrow as 10 μm in diameter. In this test, a six-layer polyethylene terephthalate laminate as described above survived more than 3,400 flex cycles in liquid nitrogen without developing through pinholes — performing significantly better than did a monolayer polyethylene terephthalate sheet of equivalent overall thickness.

To evaluate these materials for utility as terrestrial balloon materials, the flexing and pinhole tests were performed at room temperature. As in the liquid-nitrogen tests, the laminate performed better than did the monolayer sheet.

In a contemplated improvement on the basic laminate design, a layer (or layers) of reinforcing fabric would be laminated with the layers of polymeric film and layers of adhesive. At the time of reporting the information for this article, evaluation of candidate materials for use in such fabric-augmented laminates was in progress.

*This work was done by Andre Yavrouian, Gary Plett, and Jerami Mannella of Caltech for* **NASA's Jet Propulsion Laboratory**. *Further information is contained in a TSP (see page 1).*
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