KEEPING DENDRITES AT BAY WITH NUMERICAL SIMULATION

Numerical simulation drives the development of new approaches in lithium-ion battery research.

by **SARAH FIELDS**

Lithium-ion batteries can come in the form of laminated lithium-ion batteries for mobile electronic devices, cylindrical batteries for industrial power tools, and other cylindrical batteries for energy storage systems. The R&D division of Murata Manufacturing Co., Ltd., is using multiphysics simulation to examine batteries using lithium metal as a negative electrode material.

Dendrites, needle-like growths, are a fierce antagonist to efficient lithium-ion battery functioning. Dendrites form when a current is applied to a lithium metal electrode and can cause unwanted side reactions that result in short-circuiting, drastically limiting the life of the battery.

Mitigating dendrite formation is an active area of research for the entire battery industry. Most researchers approach the problem of safety hazards and life span due to dendrite formation by changing the chemistry in some way. However, gains in this area have been painstakingly slow, prompting some researchers to take an alternative path.

When examining batteries that use lithium metal as a negative electrode material, Jusuke Shimura a R&D engineer at Murata looked to investigate the effect of changing the charging current pattern on dendrite formation.

This approach is gaining traction in the battery and energy storage world as the industry ramps up to meet the needs of an era of electrification and renewable energy.

⇨ USING MULTIPHYSICS TO MINIMIZE DENDRITES

Lithium dendrite occurs when current is applied to the lithium metal electrode, resulting in a short circuit. “In order to commercialize lithium-ion batteries with lithium metal electrodes, this problem must be solved,” says Shimura.

The key to his approach was identifying a current pattern for charging that would minimize the growth of lithium dendrites. This approach works because at the off-time between pulses, the concentration gradient at the electrode interface decreases, minimizing dendrite buildup. Also, introducing reverse pulses in the current pattern plays an important role by repeatedly dissolving formed dendrites.

To capture the electrochemical effects over his geometry, Shimura enlisted the battery modeling capabilities of COMSOL Multiphysics®. He used a combination of experimental evidence and simulation to determine the best charging pattern.

Many researchers have been exploring this challenge from a chemical and material perspective. To make strides in this area, Shimura wanted to establish a baseline understanding of his physical system experimentally. It was important

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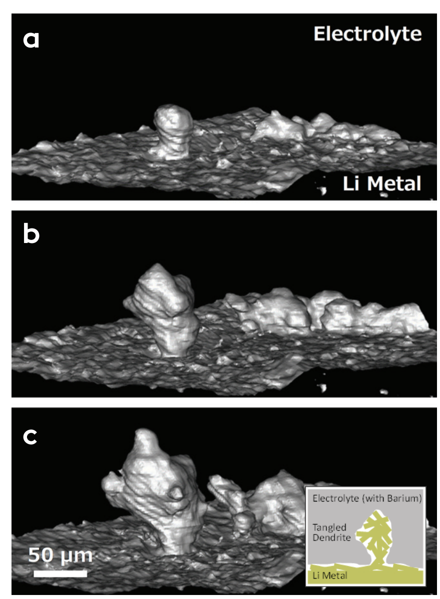

FIGURE 1. X-ray computed tomography (CT) results showing that the surface of electrolyte membrane is pushed up by lithium dendrites due to flowing current of 50 μA/cm^2 for 6 h (a), 13 h (b), and 20 h (c).

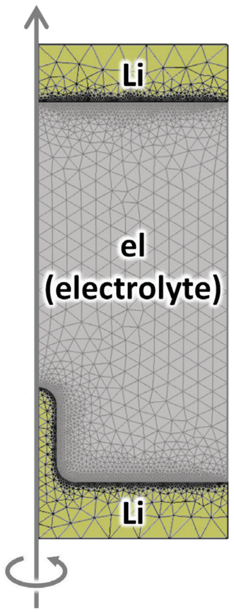

FIGURE 2. Mesh of the lithium-ion battery geometry.

for him to understand the shape of dendrite formation over time. To accomplish this, he created an X-ray CT-compatible laminated cell that contains a contrast agent in its electrolyte membrane, and visually measured the formation of dendrites over time (Figure 1).

"I created a laminated cell that could be imaged with X-ray computed tomography, so that I would know where the dendrites are forming. Then, I used COMSOL® to find the best pulse pattern of charging to limit dendrite growth based on the shape and the size of the formed dendrites," explains Shimura.

With the data from the X-ray computed tomography Shimura created a model of a lithium metal cell and analyzed the effect of changing the current pattern. The results showed how much lithium metal precipitated onto the dendrite (Figure 2).

Using multiphysics modeling, Shimura evaluated various current patterns to determine the current pattern with the slowest rate of dendrite formation (Figure 3). This method allowed him to examine which has more lithium deposition — the electrode surface with planar diffusion (bottom part of Figure 3) or the dendrite with spherical-like diffusion (left part of Figure 3) through one cycle of the pulse pattern.

He ultimately found that a repetition of reverse pulse for 20 seconds, off-time for 10 seconds, forward pulse for 20 seconds, and off-time for 10 seconds resulted in the least dendrite growth (Figure 4).

"With this pattern, we saw the growth rate of dendrites becomes less than one-third. As we expected, this was accomplished solely by changing the charging pattern — the chemistry stayed the same," Shimura explains.

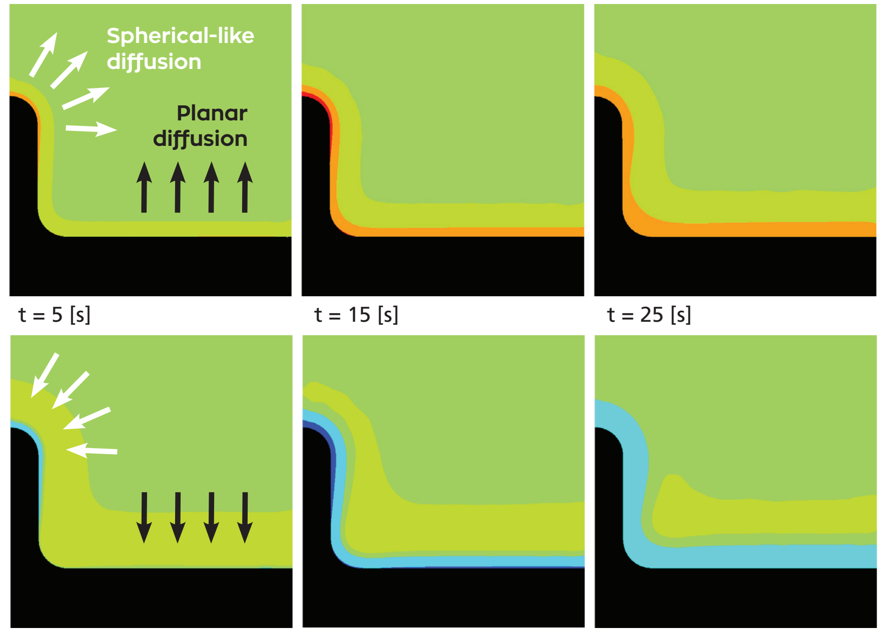

FIGURE 3. Simulation results of the dendrite growth with different pulse charging patterns.

Shimura's simulation was based on the experimentally determined size of the dendrite. It made use of the battery modeling capabilities of COMSOL Multiphysics that enlist the concentration-dependent Butler-Volmer equation to model the reactions of the electrodes and coupled diffusion-migration equations to model the lithium-ion transport.

⇨ DEVELOPING THE BATTERIES OF THE FUTURE

Using simulation, Shimura found the best pulse pattern to charge a lithium-ion battery with a lithium metal electrode. Compared to applying direct current, this approach improved the lifetime of the battery more than three times. "Thanks to COMSOL, we were able to show with a first-principles-based simulation that the optimized charging pattern improved the lifetime of the battery," Shimura says.

In the future, Shimura sees multiphysics simulation playing a continuing role in maintaining the fast pace of their research and concludes: "We look forward to continuing to use COMSOL to bring the advantages of optimized charging patterns to batteries on the market." ❖

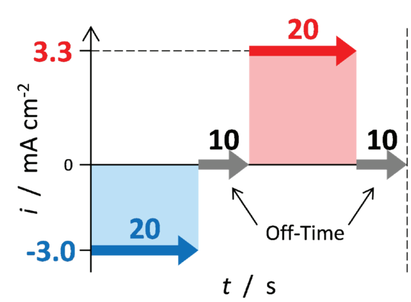

FIGURE 4. This pulse pattern was determined to be the best by finite element method simulation for the laminated cell. With the optimized current pattern, it is easier to dissolve lithium from the dendrite and more difficult to deposit lithium on the dendrite.

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