Flemish Research Institute for Technology (VITO), Belgium

DEVELOPING A NOVEL BATTERY MODEL TO ANSWER CLASSICAL CHEMISTRY QUESTIONS

Researchers at the Flemish Institute for Technical Research (VITO/EnergyVille) and KU Leuven developed a pseudo-three-dimensional model of a semisolid flow battery to find reliable answers to their design questions, such as how flow rate affects particle discharge and how cell voltage changes during the discharge process.

by **BRIANNE CHRISTOPHER**

The development of any process, component, or device involves some level of trial and error — nothing is perfect the first time. When it comes to the modeling approach itself, the same sentiment applies. Take, for instance, the modeling of a semisolid flow battery (SSFB), an innovative type of flow battery that is similar to the vanadium redox flow battery (VRFB), but involves a liquid electrolyte that carries solid particles. Up until recently, literature pertaining to SSFBs was sparse.

Kudakwashe Chayambuka, currently a PhD researcher copromoted by Grietus Mulder at the Energy Technology unit at the Flemish Institute for Technical Research (VITO/EnergyVille), along with Xochitl Dominguez, senior scientist at VITO, and Professor Jan Fransaer of the Catholic University of Leuven, set out to address this research gap in SSFB modeling.

Early research into SSFB systems used models that considered diffusion and convection as transport mechanisms occurring within the active particles. The problem? This assumption is both physically and conceptually wrong. "These models assume convective flow when the charge is contained inside flowing particles," says Chayambuka. "The equations of the original model do not hold up, and are not physical," says Fransaer, calling the model "fishy."

"We attempted to model the proper physics," continues Chayambuka. In this case, "proper physics" refers to the fact that molecular diffusion is the only transport mechanism occurring inside the solid active particles of an SSFB. Their bulk movement is not related to this molecular transport mechanism. The team developed a novel way to model an SSFB that could accurately account for its behavior and surrounding physics.

» BATTLE OF THE BATTERIES

Flow batteries are able to separate (and independently scale up) their power generation and energy storage capacity. So what makes a semisolid flow battery (Figure 1) so special? "SSFBs are very interesting, and very difficult to realize. There's no limit to the amount of energy that can be stored," says Fransaer. This type of battery is beneficial in many applications due to its high volumetric energy density. In fact, they offer 10 times the storage capacity in volume of existing vanadium redox flow batteries (VRFBs).

When based on the same materials as Li-ion batteries, SSFBs provide the highest energy density theoretically, but there are some drawbacks, including a high cost to make and an increased risk of toxicity. SSFBs made with a nickel-metal-hydride (NiMH) material include an aqueous electrolyte of potassium hydroxide to sidestep these issues.

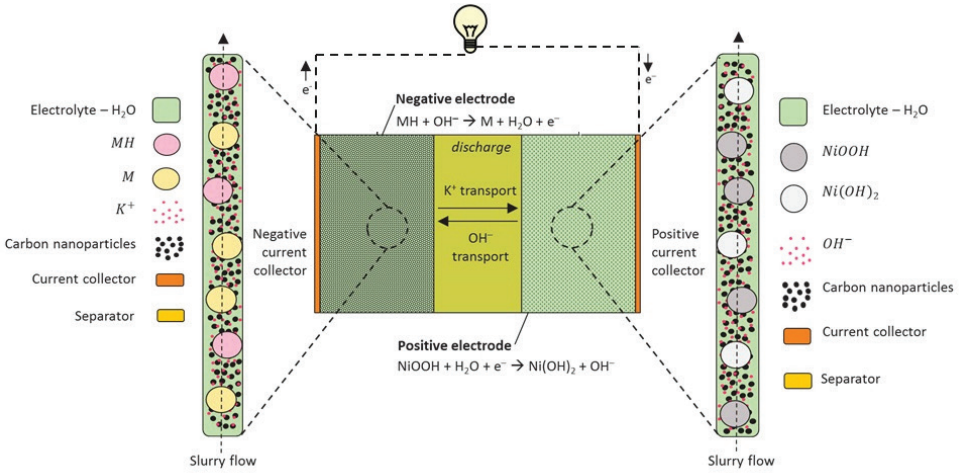

FIGURE 1 A schematic of a semisolid flow battery.

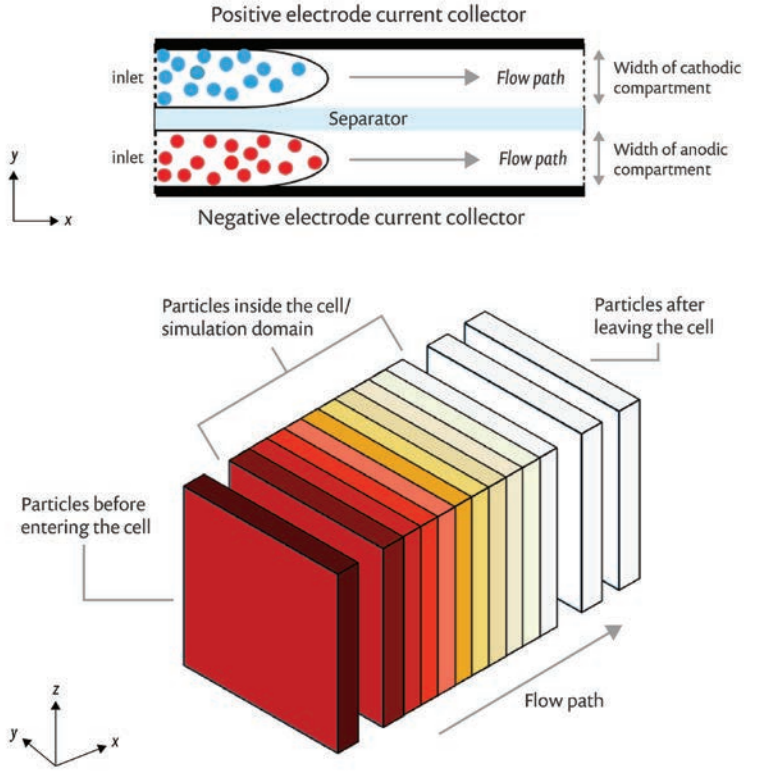

FIGURE 2 The P3D model of the SSFB.

No matter the type of SSFB, there is a major design challenge to address: Researchers need an electrochemical model that accurately describes the kinetic and transport processes occurring within the design. That is where the research group — and their novel modeling approach — come into play.

BATTERY MODELING: NOW IN PSEUDO 3D

The researchers realized that to successfully model SSFBs, they needed to be able to correctly account for the interactions between macroscale and microscale domains, as well as multiple physical processes, simultaneously. "SSFBs are very complex systems compared to other batteries. For instance, you need the right viscosity for the slurries," says Dominguez. "To predict what's happening, you need to model it. Experiments would take too much time and be too complex."

The group found that the COMSOL Multiphysics® software offers the multiphysics and multiscale capabilities their research calls for. In addition, the accurate and efficient electrochemical modeling that is possible in the COMSOL® software facilitates the optimization and scaling up of NiMH SSFB systems. "Simulations like this are really only possible with COMSOL," says Mulder.

Aside from the need for both multiphysics and multiscale modeling, SSFBs present another unique modeling challenge. Because of the active particles involved in the battery, the model needs to include particle tracing. However, you cannot couple a hydrodynamics analysis with a full particle-tracing approach, because the two studies are not compatible. The researchers tackled this problem in a two-step approach. First, they modeled the electrode movement of a nonflowing SSFB system in 2D (Figure 2). The 2D model acted as a first approximation where they could select optimized parameters, such as the concentrated and dilute solution theories for the electrolyte, material balance in the solid active particles, current balance, reaction rate, and model geometry.

Next, the researchers extended the 2D model into the pseudo 3D (P3D) model for flowing SSFB systems. "We wanted to make a nearly particle tracing model that includes physics discretized in the time domain; then stop and solve, update the position of the particles, and start again to generate proper results," says Chayambuka. "We needed a P3D geometry to model the entire flow of the battery." To do so, the team determined all of the dependent variables in separate domains as well as the associated variables that needed to be made available in the different geometries at their corresponding coordinates. "The extrusion operator feature in COMSOL Multiphysics made it simple to link the 2D and 3D domains," he says. The extrusion coupling functionality also enabled them to map the variables between separate geometries at every time step in the simulation.

Using the P3D model, the team was able to account for hydrodynamic effects in the SSFB, such as transport in the electrolyte through the Navier–

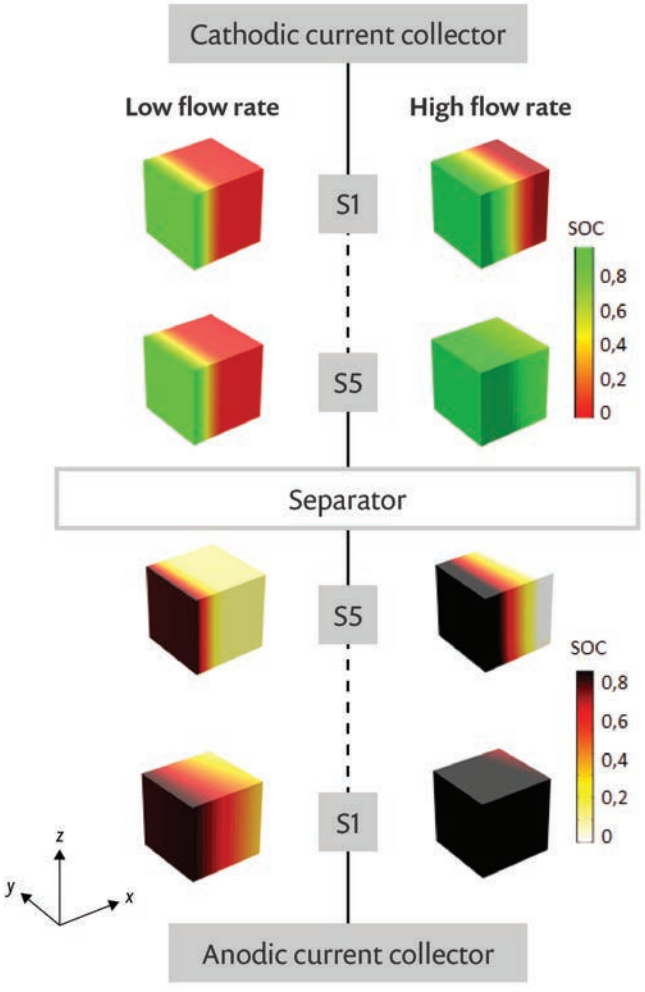

FIGURE 3 Comparison of low-flow-rate and high-flow-rate SOC distributions in a P3D NiMH SSFB model.

Stokes equations for incompressible Newtonian fluid, as well as the transport in the solid phases, including the hydrogen intercalation process modeled by pure diffusion. The team solved the time-dependent diffusion equation inside the active particles using partial differential equations (PDEs).

The researchers also found the LiveLink™ *for* MATLAB® interfacing product particularly helpful. Before introducing LiveLink™ *for* MATLAB® into their modeling workflow, the researchers did not have an automated P3D process. This meant that they had to repeatedly run the simulation, change the particle position, and then start all over again. This process was fine when they were initially starting the project, but the group soon found that it was taking a long time to find the results they needed — and this method was also more prone to errors. When they later introduced the LiveLink™ functionality into their process, Chayambuka says "it became so much easier to generate results, and we do not have to be behind a computer the whole time."

> **"To predict what's happening, you need to model it. Experiments would take too much time and be too complex."**
>
> — XOCHITL DOMINGUEZ, SENIOR SCIENTIST AT VITO

» FLOW RATE, STATE-OF-CHARGE, AND ENERGY OUTPUT

Through the results of the 2D model, the researchers found that not all of the SSFB's available charge is evenly exhausted. In fact, the extent of each particle's discharge depends on its position. The P3D model showed the researchers how the flow rate of the battery affects particle discharge, an important factor for analyzing the battery cells' dynamic behavior.

The team found that at high flow rates, the cell voltage remains mostly stable. As the discharge current increases, the voltage difference between the initial and steady-state voltage increases. For low flow rates, the voltage differences between the initial and steady-state stages are more pronounced (Figure 3). By understanding how flow rate affects the dynamic behavior of cells, they can design SSFBs for different flow rates and predict the steady state for given sets of initial conditions.

One of the most exciting aspects of the project is that this is the first time the flow-rate behavior of an SSFB has been shown in a model. Further, experimental SSFBs are showing similar transient profiles to those found in COMSOL Multiphysics, demonstrating the validity of the P3D model for this type of research.

» CHARGING UP THE FUTURE OF BATTERY RESEARCH

Through the P3D model, the research team demonstrated a novel way to model SSFB behavior. With this model, they were able to visualize the relationship between hydrodynamic and electrochemical phenomena, providing a new way to explore the design of different types of batteries. Next steps include introducing phase change effects in the model materials, introducing non-Newtonian behavior and validating the simulated flow field with experiments using carbon-water suspensions with the same rheological behavior as the electrolytes.

"Our hope is to apply this model to other types of flow batteries and test other chemistries, which would be interesting," says Chayambuka. Further, "this kind of model can be extrapolated to other systems, because they use the same principles," says Dominguez. One example she gives is the particle-based system of wastewater treatment.

The group hopes that by continuing their work, they will be able to realize an experimental system to validate the SSFB model, which would generate more interest and funding so that they can look into more ways of modeling energy losses and optimized conditions. Improved battery designs, and a better understanding of how they work, can improve how battery manufacturers store energy and generate power.