Materials science

Ion dynamics in battery materials imaged rapidly

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An imaging method has been developed that tracks ion transport in functioning battery materials in real time, at submicrometre scales — offering insights into how to design batteries that charge in minutes. **See p.522**

The most important materials in lithium-ion batteries are the 'active' particles that store and release lithium ions during charging and discharging, because they store the energy in these devices. To design batteries for any potential application, scientists need to understand the ion dynamics in the active particles. However, conventional methods for studying lithium-ion dynamics cannot track, at submicrometre resolution, the rapid changes occurring in batteries that charge in minutes. These are being developed for emerging applications such as fast-charging vehicles and flying taxis. On page 522, Merryweather *et al.*[1] report a technique that can visualize such fast dynamics.

Lithium-ion batteries consist of two porous electrodes (positive and negative), which are made up of active particles, carbon and a binder material. The carbon provides necessary electron conduction, and the binder holds the other materials together like a glue. The batteries also contain an electrolyte, which provides a conduit through which ions can move from one electrode to another.

Battery applications can be categorized in terms of their operation time — for example, portable electronics require batteries that last for 10 hours or more, and electric vehicles should be able to drive for 6–8 hours. To track the internal ion dynamics of batteries for each of these operations, researchers need to image the associated physical and chemical interactions at least ten times as fast as the operation time. This is analogous to selecting a camera shutter speed that is suitable for filming sport — if the shutter speed is too slow, the camera produces blurry pictures. In the context of batteries, the physical aspects of interest are the geometry of the active particles and the structure of the porous electrodes, whereas the key chemical process is the evolution of ion concentrations in the active particles and the electrolyte.

Every battery-imaging technique has its own characteristic image-acquisition time — this determines which battery operations can be tracked accurately. Previously available techniques[2–8] take a few minutes to acquire an image, and can therefore capture only processes that occur over several hours.

Merryweather *et al.* have customized an optical microscopy technique, previously used in biology[9], to track the movement of lithium ions in the active materials of batteries. In this approach, a laser beam is shone at electrochemically operating battery particles as they store or release lithium ions, and the scattered light is analysed. The local concentration of electrons in these particles changes as more lithium is stored, which in turn alters the scattering pattern. Therefore, the time evolution of the scattering signals at each position on a particle correlates with the local change in lithium concentration (Fig. 1).

Notably, the image-acquisition time for Merryweather and colleagues' technique is less than 1 second, which allows examination of much faster processes than was previously possible. However, having a short acquisition time is not the only requirement when studying battery function. Imaging techniques must also be able to study batteries during operation and have a reasonable spatial resolution — submicrometre resolution is needed to track what happens in an active particle. The authors' technique meets this requirement, too. Moreover, the technique can map ion dynamics at the electrode scale, by comparing the evolution of ion concentration in active particles that are spatially separated in the electrode.

Almost all active materials that store lithium or other ions undergo electronic changes as the ion concentration varies, and are therefore amenable to study by this technique. The time variation of ion concentration in active particles is poorly understood, because conventional techniques can not directly track changes in local concentration throughout a particle during fast operation. By solving this problem, Merryweather and co-workers' method will help researchers to validate the hypothesized mechanisms of ion transport in these materials (see ref. 10, for example).

It should be noted that the spatial resolution of the authors' imaging technique is constrained by a fundamental limit defined by the wavelength of the light used, which means that shorter wavelengths are needed to resolve smaller details. The resolution is about 300 nanometres in the current study. Another caveat is that scattering is the cumulative effect of light interacting with just the first couple of atomic layers of the particle. This approach therefore captures only the ion dynamics in the 2D plane associated with these atomic layers. By contrast, 3D information can be obtained using slower methods, such as

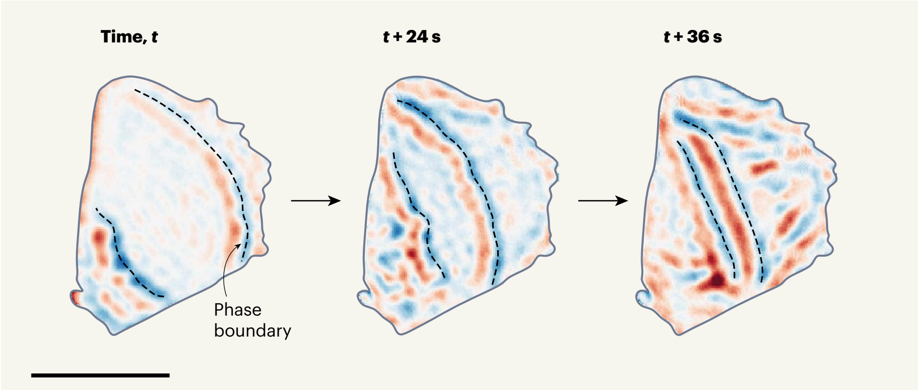

Figure 1 | Images of a functioning battery particle. 'Active' materials in battery electrodes store and release ions during charge–discharge cycles. Merryweather *et al.*[1] report an imaging technique that uses light scattered from functioning active particles to track changes in ion concentration in real time. In their approach, the scattering intensity changes with local ion concentration, and so the evolution of scattering patterns over time represents the ion dynamics of the system. Here, the colours of the contours represent the change of scattering intensity over the previous 5-second period as more ions are stored in the particle: red indicates an increase in intensity; blue indicates a decrease. The changing patterns correlate with the transition of one phase of the material to another. Broken black lines indicate the boundaries between phases when a central domain consisting of one phase shrinks, and surrounding domains of another phase expand. Scale bar, 5 micrometres. Images from Fig. 5e of ref. 1.

X-ray tomography[3,5].

It will be exciting to take the authors' findings for individual particles further and study porous electrodes at the far-from-equilibrium conditions associated with rapid charging. For example, it was hypothesized[11] last year that inhomogeneous porous-electrode structures result in non-uniform distribution of lithium in electrodes when batteries are charged in minutes. Merryweather and colleagues' technique could act as a test for such predictions.

This method could also be used to examine solid electrolytes — battery materials that are interesting, but poorly understood. If light scattering from solid electrolytes changes with local ion concentration as it does in active materials, then the technique could be used to map how the ion distribution in such electrolytes changes when an electric current passes through them. Optical scattering might be equally useful for studying other systems that involve coupled ion and electron transport, such as catalyst layers in fuel cells and electrochemical gas sensors.

In the future, it should be possible to quantify the relationship between the scattering response and lithium-ion concentration by conducting meticulous scattering experiments using active particles that are compositionally uniform. This correlation could then be used to convert scattering signals to local concentrations. However, the relationship will not necessarily be the same for different materials, and might be difficult to identify in each case. Machine-learning techniques could be used to streamline the determination of these relationships and to automate analysis of scattering responses[12].

The authors' imaging technique also opens up the prospect of simultaneously tracking the chemical and physical (geometric) changes that occur in active particles during battery operation. The time course of scattering in a particle would reveal local changes in lithium concentration, and the difference between the scattering from a particle and that from other materials in a battery (such as the binder or electrolyte) could be used to determine the particle shape and how it evolves with time. Such experiments would revolutionize the study of active materials (such as silicon) that appreciably expand and contract as the lithium concentration changes within them. Materials of this type store much more energy than currently used active materials do, and their use might reduce battery weight. This would be particularly useful in electric vehicles, because it would enable longer driving ranges.

Merryweather and colleagues' research offers previously inaccessible insights into battery materials operating at far-from-equilibrium conditions. Their method for directly observing changes in active particles during operation will complement existing approaches, in which internal changes are inferred from destructive testing of batteries. It could therefore revolutionize the battery-design cycle.

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