

Neutron studies of materials in real operating batteries are helping to improve their performance

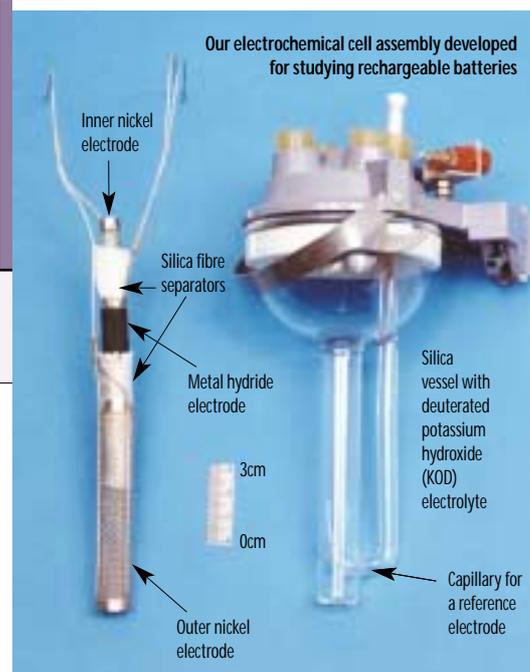
Towards a better battery

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Materials for storing electrical energy have been the subject of intense research in recent years, as a result of the rapid development of portable electronic equipment such as mobile phones and laptop computers. These devices depend for their operation on rechargeable batteries, which work by converting chemical energy stored in electrodes, into electrical energy, via electrochemical reactions. These reactions correspond to the loss or gain of electrons and ions in the electrode materials. The electrical current is carried by electrons outside the battery and by ions (charged atoms) in the electrolyte between the electrodes inside the battery. The electrochemical reactions are reversible, so when all the energy has been delivered the battery can be charged up again from an external electrical source.

There are two types of rechargeable batteries currently used in portable devices: nickel-metal hydride (Ni-MH) batteries, which involve hydrogen ions, and are replacing the kind based on nickel and toxic cadmium; and lithium-ion batteries.

These batteries still have shortcomings, however, and are continually being improved in terms of performance – power capacity and output, and lifetime (the number of charge-discharge cycles the battery goes through without degrading). One of the keys to making improvements is a detailed understanding of the crystal structure of the electrodes and how the ions diffuse in it. Here, neutron powder diffraction (see p.4) is a powerful tool and gives more information than X-ray diffraction. Neutrons can easily penetrate the sample so



as to give accurate information about the bulk material, and the hydrogen and lithium ions trapped in the electrodes scatter neutrons well so they can be readily located.

Studies in real time

We have been carrying out extensive studies on nickel-lanthanum hydrides used as electrode materials in Ni-MH batteries. The continual charge-discharge of the standard electrode involves a cyclic transformation between two crystalline phases called α and β . These have unit (cell) volumes that differ by 20 per cent, which induces heavy constraints in the material and causes its crystal structure to fragment. That leads to surface corrosion and reduces the battery lifetime.

We carried out experiments using the D1B diffractometer at ILL, which followed the structural changes during cycling on different electrode materials. These experiments showed that a transitory intermediate γ phase with a cell volume between that of the α and β phases may appear (see left) for some peculiar alloy compositions. The appearance of this intermediate γ phase at the boundary between the α and β phases significantly reduces the constraints during the cycling process, leading to a better lifetime.

Another problem is related to the high charge/discharge rates required by many applications of these batteries. Using a newly designed electrochemical cell (above), with an electrode arrangement similar to that in real batteries – in conjunction with the high neutron flux available on the D20 diffractometer – we could also follow changes in the electrode at high cycle rates. We showed that the cycle rate was limited by the speed of associated transitions in the electrode's crystal form, rather than the rate of diffusion of hydrogen ions in the electrode material.

The next challenge will be similar studies of lithium-ion battery electrode materials. ■



PHD

A 3D plot of the neutron diffraction patterns recorded for a metal hydride electrode as it discharges. It shows how different crystal phases (α , β and γ) form over the cycle

