

BUILDING BETTER CATHODES FOR RECHARGEABLE, EARTH-FRIENDLY BATTERIES

A new nanostructured material has qualities necessary for good cathodes in next-generation rechargeable batteries. Researchers at Argonne, The University of Chicago, and the Illinois Institute of Technology mixed iron oxide nanoparticles and carbon nanotubes to create a cathode that allows fast charge transfers and cyclability in a sodium ion battery. Using x-rays from two beamlines at the APS, they monitored the material as ions moved into and out of the cathode's crystal lattice. Because iron oxide, carbon, and sodium are all abundant materials, this is a promising route to developing efficient, cost-effective, rechargeable batteries. These results were the cover subject of *Chemistry of Materials* **25**(7), 2013.

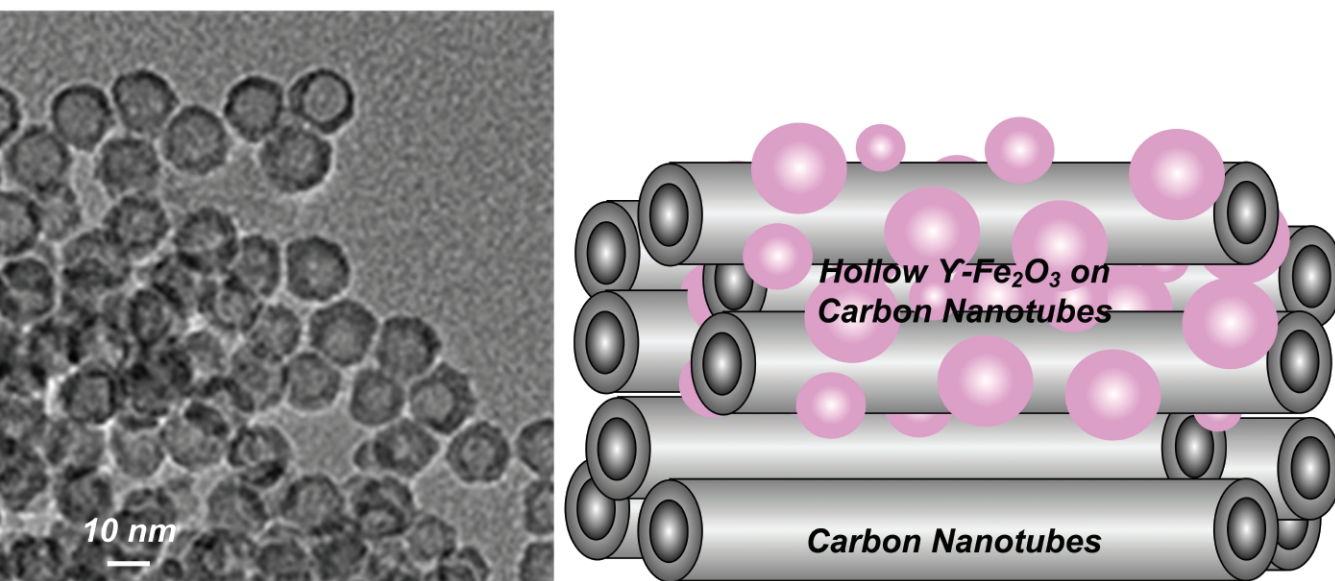
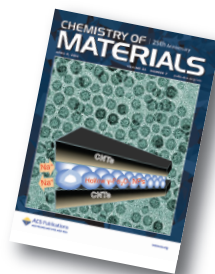


Fig. 1. Transmission electron micrograph of the hollow iron oxide nanoparticles (left) and depiction of the electrode structures (right). The electrodes were used to test the intercalation and deintercalation of Na^+ ions in hollow iron oxide nanoparticles that were found to have a high concentration of iron vacancies.

Portable electronics and hybrid cars are powered by lithium ion (Li-ion) batteries. The technology provides desirable charge capacity and cyclability at a commercially viable price and weight. But Li is a limited resource, whereas the demand for batteries continues to grow. Sodium (Na)-ion batteries utilize materials that are more abundant than Li, but are not as well developed. Many cathodes (which attract positively-charged ions from the electrolyte solution in the battery) designed for Li-ion batteries perform poorly in batteries that use the larger Na ions.

A test battery built using Argonne's Center for Nanoscale Materials (CNM) from a cathode made of hollow iron oxide nanoparticles and carbon nanotubes was subjected to multiple charge and discharge cycles. The researchers then took electron microscope images, again at the CNM, of the materials before and after charging. Using synchrotron x-rays they could also monitor changes in the cathode while the battery cycled.

To understand what happens when the Na ions move into the iron oxide nanoparticles, the researchers used two x-ray absorption spectroscopy methods that allowed them to study the local structure around certain elements in the cathodes: x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS). They used XANES to figure out the oxidation state of the iron and thus determine the concentration of vacancies (areas into which Na ions could move) in different positions in the crystal lattice. The XANES and EXAFS measurements were conducted at the MR-CAT 10-ID-B beamline at the APS.

The researchers also used x-ray diffraction to study changes in both the crystalline lattices and vacancies. These measurements were performed at the GSECARS beamline 13-ID-C,D at the APS.

Electrodes usually fail because of damage to the material. As ions move into and out of the cathode, delivering charge, the cathode swells or shrinks,

which can literally pulverize the oxide electrode. As damage accumulates, the pathways that guide charge out of the battery are also damaged, so over a number of cycles the efficiency of the battery declines. To combat this damage, the researchers used CNM's synthesis facilities to create hollow nanoparticles — which tolerate volume changes well — sandwiched between carbon nanotubes, providing good electrical connectivity even if the charge-accepting material is damaged. Using XANES measurements, they discovered many cation vacancies in the iron-oxide structure, about four times higher than in most cathode materials.

Nanoparticles made up 45% of the electrode by weight. The researchers found that the Na ions enter the vacancies faster than iron oxidizes. Thus, charge transfers from the electrolyte to cathode faster than the chemical reaction that would change the cathode material from an inverse spinel to a rock salt structure. They tested the speed of charging and the electrode's capacity (in other words, how much electric charge can be provided by a certain weight of material). The electrode had a large and reversible capacity of 189 mAh/g. But many good cathodes for Na-ion batteries fade quickly, so how does this one stack up to repeated charging? Strikingly, after 500 cycles of quickly draining a lot of charge (99 mAh/g) from the test cell, the researchers found that the cathode retained its capacity.

They discovered that the Na ions move inside the hollow nanoparticles and do not damage the crystal structure of the cathode. In fact, the crystal structure improved with use. Also, when subjected to many cycles at high current rates, the capacity increased! They believe that the vacancies become organized into channels that make it easier for Na ions to move through the structure.

This is the first Na cathode material that shows high-rate performance while maintaining capacity, to the best of the researchers' knowledge. Therefore, the hollow nanoparticles sand-

wiched by carbon nanotubes offer an Earth-friendly and efficient cathode material for Na-ion batteries. The researchers continue to investigate the cathode by changing the concentration of vacancies via doping the ferrous oxide with multivalent cations.

— Yvonne Carts-Powell

See: Bonil Koo^{1*}, Soma Chattopadhyay³, Tomohiro Shibata³, Vitali B. Prakapenka², Christopher S. Johnson¹, Tijana Rajh¹, and Elena V. Shevchenko¹, "Intercalation of Sodium Ions into Hollow Iron Oxide Nanoparticles" *Chem. Mater.* **25**(7), 245 (2013).

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10-ID-B • MR-CAT • Materials science, environmental science, chemistry • X-ray absorption fine structure, time-resolved x-ray absorption fine structure, micro x-ray absorption fine structure, microfluorescence (hard x-ray) • 4.3-27 keV, 4.3-32 keV, 15-90 keV • On-site • Accepting general users •

13-ID-C,D • GSECARS • Geoscience, environmental science • Inelastic x-ray scattering, micro x-ray absorption fine structure, microdiffraction, x-ray absorption fine structure, microfluorescence (hard x-ray), high-pressure diamond anvil cell, high-pressure multi-anvil press • 4-45 keV • On-site • Accepting general users •