Nanomaterials and lithium rechargeable batteries

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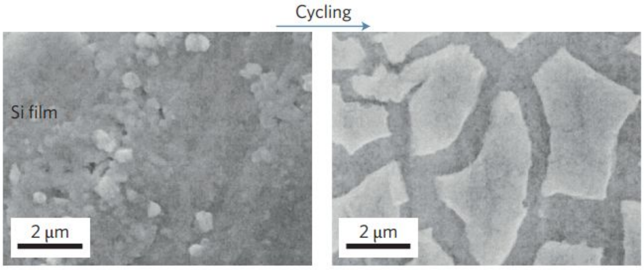

SEM images of a deposited 250 nm Si film on Cu before (left) and after (right) 30 discharge/charge cycles between 1.2 and 0.02 V at 2.5 C. Credit: (c) *Nature Energy* (2016). DOI: 10.1038/nenergy.2016.71

(TechXplore)—In a review article in *Nature Energy*, Yongming Sun, Nian Liu, and Yi Cui from Stanford University survey how nanomaterials have advanced the field of lithium rechargeable batteries and what obstacles still need to be overcome to make high-capacity rechargeable lithium batteries a practical energy source.

Many electronic and portable devices make use of lithium batteries. Current lithium batteries are much lower in capacity than what they could potentially be. Many researchers have attempted to design high-capacity lithium batteries that are inexpensive and rechargeable over many cycles. However, the battery chemistry that offers higher storage capacity also comes with prohibitive drawbacks. To get around these drawbacks researchers have turned to nanomaterials for solutions.

The first major drawback to high-capacity lithium batteries is, during the process of discharging and re-charging the battery, the electrode materials exhibit a dramatic change in volume. This eventually leads to electrode degradation. As the electrode cycles through gaining and losing material, it will crack and fracture.

Nanomaterials offer possible solutions at both the particle-level and at the electrode-level. Nanomaterials tend to be more resistant to mechanical degradation than other materials. One solution is to use nanoparticles or nanowires that are below the critical fracture size for a lithium electrochemical cell.

At the electrode-level, nanomaterials can be used as a kind of "glue" to hold the anode particles together. The constant fracturing, cracking, and re-forming of the active material leads to electrical disconnection, but the "glue" can keep the active materials electrically connected increasing the lifetime of the lithium cell. Amorphous silicon glue has been used to bind Si nanoparticles on an electrode.

Other solutions to the large volume changes have included forming nanocomposites or entrapping key compounds, such as sulfur, using yolk-shell nanostructures.

One problem that has plagued lithium battery cells is the accumulation of a precipitate layer between the solid anode and the electrolyte. Lithium solids will form on the anode surface, creating an electronic insulating layer that still conducts lithium ions. This is knowns as the solid-electrolyte interphase, or SEI. Because of the volume changes that occur upon charging and discharging the SEI becomes unstable and cracks exposing the electrode. This causes more solid growth until eventually the active materials are consumed or degraded.

Solutions to the unstable SEI problem include a nanostructured interface, encapsulating the electrode to create a stable interface, or incorporating electrolyte additives. The authors of this review have used Si-SiOx double-walled nanotubes to form a stable SEI layer.

Lithium anodes, in particular, are prone to forming dendrites between the anode and the electrolyte. Once dendrites grow to the point that they connect the electrodes, the battery will discharge. Solutions to this include constructing a protective coating of carbon nanospheres, constructing an artificial SEI layer, or adding compounds to the electrolyte that inhibits dendrite growth.

A battery would ideally be able to transport electrons and ions quickly and efficiently. This means highly conductive pathways for electrons and short distances for ions to travel. Nanoparticles are smaller than other particles and are therefore, conducive to shortening electron and ion travel distances. Researchers have used Si-C nanofibers, Sn/C composite spheres, and graphene materials to enhance electron and ion movement at the particle level. They have also looked at incorporating various types of nanoarchitectures onto a metal current collector. Finally, they have also investigated current collectors that are made of networked materials such as graphene.

In general, as the authors point out, materials used in any high-capacity electrode that undergoes volume changes will have atom or molecule diffusion loss. This loss is due to solid morphology changes from fracturing or volume expansion and/or phase changes such as the production of solids. For example, lithium-sulfur batteries often produce polysulfide intermediates that eventually degrade the sulfur electrode.

Nanomaterials such as porous carbon or yolk-shell nanostructures allow for physically trapping the polysulfide intermediates. Another option is to chemically confine the intermediates on an electrode surface using adsorbent nanomaterials.

While nanomaterials offer potential solutions to typical high-capacity lithium battery problems, they have a few drawbacks. First, when trying to pack smaller particles (i.e., nanoscale instead of microscale) together, the overall surface area will increase. More surface area means that more electrolyte solution is consumed at the SEI. This also increases the likelihood of unwanted side reactions.

Additionally, nanoparticles have a low packing density. That extra space between particles results in a low tap density, which is related to the extent that an electrode's volume will change. And, finally, producing nanoparticle materials is still prohibitively expensive to be practical on a commercial scale.

More information: Yongming Sun et al. Promises and challenges of nanomaterials for lithium-based rechargeable batteries, *Nature Energy* (2016). DOI: 10.1038/nenergy.2016.71

Abstract

Tremendous progress has been made in the development of lithium-based rechargeable batteries in recent decades. Discoveries of new electrode materials as well as new storage mechanisms have substantially improved battery performance. In particular, nanomaterials design has emerged as a promising solution to tackle many fundamental problems in conventional battery materials. Here we discuss in detail several key issues in batteries, such as electrode volume change, solid–electrolyte interphase formation, electron and ion transport, and electrode atom/molecule movement, and then analyse the advantages presented by nanomaterials design. In addition, we discuss the challenges caused by using nanomaterials in batteries, including undesired parasitic reactions with electrolytes, low volumetric and areal energy density, and high costs from complex multi-step processing, and their possible solutions.

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