

Nanostructured Lithium Sulfide/Silicon Electrode Design Quadruples Theoretical Specific Energy of Rechargeable Batteries

With recent advances in high-capacity anodes, the limiting factor in producing rechargeable batteries with a high specific energy (for use in electric vehicles and portable electronics) now stems from the relatively low specific capacity of the corresponding cathodes. While sulfur-based cathodes in combination with lithium anodes have the potential to overcome these capacity limitations, the use of elemental Li as the anode leads to serious safety concerns—Li dendrites form during cycling and can penetrate the thin polymer layer separating the two electrodes, leading to short circuits and potential explosions. Y. Yang, A.T. McDowell, A. Jackson, and colleagues at Stanford University, however, combat these issues by pairing sulfur's lithiated counterpart (Li_2S) in the cathode with a high capacity, low potential silicon nanowire anode to create a novel nanostructured rechargeable battery with a theoretical specific energy four times that of existing LiCoO_2 /graphite or LiFePO_4 /graphite systems.

As described in the April 14 issue of *Nano Letters* (DOI: 10.1021/nl100504q; p. 1486), on the cathode side of the battery depicted in Figure 1, the researchers first diffuse sulfur into the sub-5 nm pores of ordered mesoporous carbon and then convert it into Li_2S by a reaction with n-butyllithium. The ordered mesoporous carbon consists of hexagonally arranged 7–8-nm thick nanorods around 3–4 nm pores. The interconnected carbon rods act as conductive pathways, providing electronic access to the insulating Li_2S trapped within the pores while the submicrometer

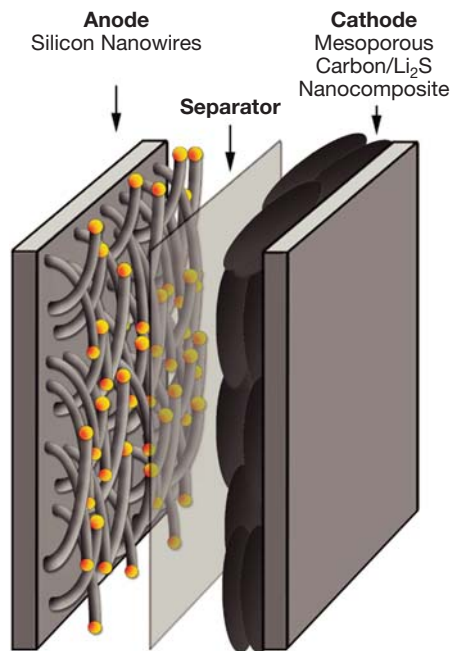


Figure 1. Schematic of the $\text{Li}_2\text{S}/\text{Si}$ battery structure: The cathode contains lithium-sulfide incorporated within the pores of ordered mesoporous carbon, and the anode consists of silicon nanowires grown onto stainless steel substrates using the vapor-liquid-solid method. Reproduced with permission from *Nano Lett.* 10(4)(2010) 1486; DOI: 10.1021/nl100504q. ©2010 American Chemical Society.

size of the carbon particles shortens Li diffusion paths—this design overcomes the slow kinetics (and poor electronic conductivity) inherent to Li_2S -based cathodes. On

the anode side, silicon nanowires are grown by the vapor-liquid-solid (VLS) method onto a stainless steel substrate. Silicon is known to have a very high theoretical capacity (4212 mAh/g) and low potential (~ 0.3 V versus Li/Li^+), and unlike previous Si-based electrodes, the nanowire architecture allows for the requisite 400% volume change associated with the insertion and extraction of Li without disintegration or significant capacity fading.

The resulting higher capacity and lower overpotential of $\text{Li}_2\text{S}/\text{mesoporous carbon}$ as compared to $\text{Li}_2\text{S}/\text{macroporous carbon}$ observed by the researchers clearly demonstrate the importance of size, morphology, and structure of the porous carbon on the corresponding electrochemical performance of the composite cathode. When examining the performance of the full battery cell at a lowered current rate (corresponding to an eight-hour discharge time), the researchers can thus far achieve an initial discharge specific energy of 630 Wh per kg of active electrode material (as compared to the theoretical calculation of 1550 Wh/kg). If the total electrode mass is considered, this corresponds to a specific energy of ~ 349 Wh/kg, which is similar to the 335 Wh/kg provided by commercial Li-ion batteries. Moreover, the researchers project that “the specific energy could reach ~ 600 Wh/kg considering the total electrode mass with further optimization of the battery.” They also said that “utilization of better electrolytes and surface modification of the electrodes are necessary to overcome the cycling behavior and capacity decay issues associated with their current design,” thereby enabling competition with well-developed Li-ion battery systems.

TIFFANY D. ZIEBELL

Sol-Gel Electrophoretic Deposition Process Improves Dye-Sensitized Solar Cells

Dye-sensitized solar cells (DSSCs) hold significant promise as a lower cost alternative to conventional silicon photovoltaics. Their ability to be fabricated using inexpensive techniques on flexible plastic substrates has attracted considerable research interest since they were first demonstrated almost 20 years ago. However, their efficiencies are limited by electron losses in the anode. Now A. Zaban, L. Grinis, and their colleagues at Bar-Ilan University in Ramat Gan, Israel have demonstrated a new low-temperature coating technique using sol-gel processing and electro-

phoretic deposition (EPD) that partially overcomes this limitation. They reported their findings in the January 22 issue of *Advanced Functional Materials* (DOI: 10.1002/adfm.200901717; p. 282).

DSSCs are based on photosensitive dyes covalently bonded to a mesoporous scaffolding of TiO_2 nanoparticles. During operation, photons from sunlight produce photoelectrons in the dye, which are then injected into the nanoparticles for transport to a conducting substrate while the dye is reduced by an electrolyte permeating the system. Electrons must travel through tens or hundreds of nanoparticles to reach the substrate, making good inter-particle electrical connections and

low recombination rates with holes in the electrolyte critical for efficient operation. Numerous approaches to overcoming these problems have been investigated involving coatings on the scaffolding, but many of them require high-temperature sintering, which would prohibit fabrication on flexible plastic substrates.

To address this problem, the researchers coated the nanoparticles using a low-temperature sol-gel EPD process based on metal alkoxides carried out from dilute alcohol solutions containing iodine, acetone, and water, at low current densities ($25\text{--}100 \mu\text{A}/\text{cm}^2$). This resulted in thin, amorphous coatings of titania, magnesia, or niobia on the mesoporous TiO_2 , which

were determined by high-resolution transmission electron microscopy to be conformal, uniform, continuous, and dense, with a controllable thickness between a few Ångströms and a few nanometers. After drying the samples for 4 h at 150°C, the team then used them to fabricate DSSCs. While niobia coatings did not improve the

cell performance, cells based on electrodes with amorphous titania coatings were up to 65% more efficient than non-coated reference cells, and bi-layer titania/magnesia coatings led to up to 113% efficiency gains. The researchers attributed the enhancements to improved inter-particle connections from the titania layer and reduced

recombination rates due to the insulating properties of the magnesia layer.

These results suggest that enhanced DSSCs fabricated by a low-cost, low-temperature technique may one day offer a competitive alternative to conventional silicon photovoltaics.

COLIN MCCORMICK

High Modulus Fluorinated Molding Materials Improve Fidelity in Soft Lithography

Molding materials used for soft lithography, a nanofabrication technique, just got a little tougher. Polydimethylsiloxane (PDMS) elastomers, typically used as a molding material to replicate feature sizes greater than 100 nm, tend to have a low elastic modulus (2.0 MPa) and low surface energy (~25 mN/m). These properties make it easy to remove the PDMS from delicate master templates. New findings, however, show that increasing a material's elastic modulus may help improve pattern transfer fidelity, especially when replicating high aspect ratio features with small spacing or periodicity. A research team including S.S. Williams and co-researchers at the University of North Carolina at Chapel Hill, S. Retterer at Oak Ridge National Laboratory, R. Ruiz of Hitachi Global Storage Technologies, and J.M. DeSimone at the University of North Carolina at Chapel Hill and North Carolina State University reported in the April 14 issue of *Nano Letters* (DOI: 10.1021/nl100326q; p. 1421) a composite molding technique that utilizes perfluoropolyether-(PFPE)-based elastomers. Williams and colleagues found that by increasing the modulus of the PFPE, smaller feature sizes could be replicated than when molds were made with PDMS.

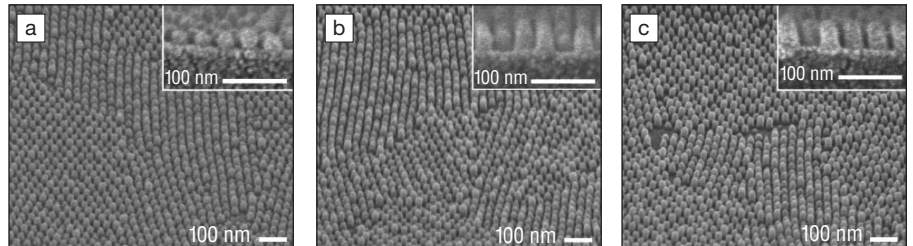


Figure 1. Trimethylolpropyl triacrylate (TMPTA) patterns formed using a variety of composite molds. TMPTA patterns made with molds composed of a low modulus material (1.4 K perfluoropolyether, PFPE) (a) demonstrated a loss in resolution while TMPTA patterns from molds made with higher modulus materials such as (b) 80:20 1.4 K PFPE/TMPTA blend and (c) PFPE-tetramethacrylate showed much higher fidelity.

“The key to high fidelity molding materials,” said Williams, “is that you need a combination of a high modulus material that retains a low surface energy.” The team systematically examined the macromonomer functionality (i.e., the number of acrylate groups per polymer chain), the molecular weight of the macromonomer, and the addition of a multifunctional crosslinking additive (trimethylolpropyl triacrylate, TMPTA). Molds with higher functionality, lower molecular weight macromonomers, or TMPTA partially substituted for PFPE showed dramatic improvements in modulus with an insignificant bump in surface energy (see Figure 1). The molds with higher modulus had

lower propensity for lateral collapse of high aspect ratio features.

Overall, the new PFPE molds improved fidelity of pattern transfer from the master to the mold and from the mold to TMPTA replicates. While previously reported PDMS molds were able to replicate 80 nm × 80 nm feature sizes with 100 nm heights, the PFPE molds were able to replicate 20 nm × 20 nm feature sizes with 40 nm heights in TMPTA. The researchers also note the ability to easily tailor the height of the flash layer, a feat that is difficult to obtain without the use of expensive equipment.

KEVIN P. HERLIHY

Magnetic Field Applied to 3D Manipulation of Alloys

The relentless drive toward increased miniaturization and better performance of microelectronic devices has necessitated three-dimensional (3D) architectures with vertical geometries. Such 3D architectures require stacked two-dimensional layers formed by photolithography or perpendicular vias for the conductive pathways. Various new approaches have been proposed to obtain such structures, including self-assembly and ink-jet printing; however, these use processes and

materials not commonly found in current microelectronics fabrication facilities.

A different issue is the current use of lead-based solders as joining materials, serving as interconnects in devices. Due to serious health concerns associated with the use of lead-based solders, lead-free alternatives are being explored, such as Sn-3.5%Ag, and are being mandated through regulations such as the Restrictions on Hazardous Substances (RoHS). Unfortunately, this lead-free material has processing temperatures 30–40°C above the melting point of 220°C,

of the incumbent SnPb alloy, which can significantly affect device performance. Now, A.G. Ramirez and her co-workers at Yale University report in the March 16 issue of the *Proceedings of the National Academy of Sciences* (DOI: 10.1073/pnas.1001410107; p. 4834) the development of tin-silver-based alloys containing iron dispersions that can be inductively heated and remotely manipulated in 3D space using a magnetic field. The iron dispersions allow for magnetically driven inductive non-contact heating, while at the same time imparting mechanical strength.