What Nano Can Do for Energy Storage

CS Nano has been attracting a large number of submissions on materials for electrical energy storage and publishing several in each recent issues (read two examples from the May 2014 issue^{1,2}). The need for more efficient storage of electrical energy at all scales, from solar and wind farms to wearable electronics like Google Glass, requires development of devices offering the high energy densities of batteries along with the long cycle lives, high powers, and short charging times of supercapacitors. This has led to a dramatic expansion of research activities at the energy frontier, but why do we need "nano" in energy storage? Indeed, there are many reasons:

- (1) Short diffusion distances make it possible to charge batteries faster or to draw high current in a short time (increase the power).
- (2) Large expansion that leads to failure and short cycle lives of microparticles can be accommodated—silicon use in Li-ion battery anodes is a good example, as nanoparticles can survive cycling. Thus, we can use materials capable of larger energy storage or increase the lifetime of currently used materials.
- (3) Transport of multivalent ions in bulk materials is slow, and use of nanomaterials can enable practical Mg- or Al-ion batteries, capable of storing much more energy than the currently used Li-ion batteries.

This list is hardly exhaustive, but it is already clear that nanostructuring of existing materials (*e.g.*, metal oxides or silicon) and development of new nanomaterials (*e.g.*, two-dimensional, 2D, carbides, and carbonitrides—MXenes³) and hybrid nanomaterials/nanostructures (*e.g.*, nanoparticles on graphene) are seen as pathways to new solutions for electrical energy storage. Nanoscale design of the structure and chemistry of electrode materials may enable us to develop a new generation of devices that approach the theoretical limit for electrochemical storage and deliver electrical energy rapidly and efficiently.

On the fundamental side, understanding nanoscale processes in energy storage materials is essential to uncover the underlying mechanisms. With this knowledge, new concepts can be formulated that will be developed into revolutionary new electrical energy storage devices and technologies.

A large variety of processes that occur during charge storage may be confusing for chemists and material scientists that are new to the field. In battery materials, conversion from one state

to another occurs at a constant potential until the phase transformation is completed. Charge storage in supercapacitors typically includes ion adsorption in the electric double-layer capacitor (EDLC) or fast electrochemical reaction at the surface of the active material (pseudocapacitors).⁴ Rapidly available surface charge without diffusion limitation is the origin of their high power density, and the absence of

Nanoscale design of the structure and chemistry of electrode materials may enable us to develop a new generation of devices that approach the theoretical limit for electrochemical storage and deliver electrical energy rapidly and efficiently.

bulk phase transformation leads to high reversibility and long life (up to 1,000,000 cycles). However, since the charge is confined to the surface, the energy densities of EDLCs are less than those of batteries (three-dimensional, 3D, chemical storage). Classical (2D) double-layer charge storage is possible on the planar surfaces of graphene aerogels or convex outer surfaces of carbon nanotubes or onions. In commercially used microporous activated carbons, ions are confined (electrosorbed) in pores. This process is significantly different than the conventional double layer and is rather similar to gas adsorption or adsorption of organic molecules from water by activated carbons, but driven by an electrical rather than a chemical potential.

Nanomaterials and hybrid nanomaterials may enable us to build energy storage devices with the energy densities of the best batteries but with the high power, fast charging, and

Published online June 24, 2014 10.1021/nn503164x

© 2014 American Chemical Society

long cycle-life features of electrochemical capacitors.⁶ We welcome papers pursuing this goal at *ACS Nano*. At the same time, we are not interested in articles presenting battery materials, like nanoparticles of metal oxides/hydroxides used in alkaline batteries, as new "high energy density supercapacitors". Materials that experience phase transformations (e.g., NiOOH to Ni(OH)₂) and show sluggish kinetics with highly nonlinear charge—discharge and redox peaks in cyclic voltammograms should not be called supercapacitors.⁵

Graphene is one of the most exciting materials being explored today, but in spite of the huge amount of data produced and numbers of papers published, it remains unclear if it will revolutionize the energy storage field or simply find niche applications. There is little reason to believe that a breakthrough in energy storage will be achieved by simply combining graphene with every single kind of nanoparticle known. Although many interesting architectures can be produced using graphene⁷ and smart electrode designs can lead to excellent performance of graphene-based supercapacitors, many other carbon nanomaterials deserve attention. A recent study suggests that no synergistic effect occurs in nanotube—graphene hybrids—the total capacitance is just a sum of capacitances of individual components. If a synergistic effect is claimed, a reason for it must be explained—ACS Nano is a nanoscience journal, after all.

When we receive manuscripts claiming extraordinary performance for a well-known material (*e.g.*, graphene) for no obvious reason, we and other experts suspect that this is due to the use of very thin or ultralight electrodes, parasitic redox reactions, and other such effects. ¹⁰ If authors claim a record in the energy storage field, they must identify and explain the mechanism and ensure that the electrochemical testing is done correctly—*ACS Nano* publishes comprehensive papers for precisely this purpose, so authors can, and should, go into detail.

At ACS Nano, we especially welcome papers addressing:

- Atomistic and multiscale modeling that enables evaluation/selection and even design
 of new materials, architectures, and processing methods expediting the development
 of new energy storage concepts. Computational studies can provide direction to the
 synthetic efforts and rule out less promising avenues, expediting the research and
 development of new materials.
- 2. Understanding charge transfer and storage at electrochemical interfaces at the nanoscale. As a field, we are still missing comprehensive understanding of how the local electronic structure of the electrode material, electrostatic interactions, and charge transfer between the electrode and electrolyte govern the charge storage mechanism and ionic transport.
- 3. Fundamental gaps in the understanding of atomic- and molecular-level processes that govern the operation, performance, and failure of the current energy storage devices.
- 4. In situ and in operando studies of nanoscale processes using a variety of microscopy and spectroscopy techniques—the development and use of new techniques would be especially attractive.
- 5. Nanoscale material architectures that enable efficient charge and ion transport and maximize the use of active materials. Conformal decoration of large-surface-area electrodes and current collectors with active insertion hosts or organic redox moieties may provide higher capacities for batteries and pseudocapacitors. This will require nanometer thicknesses of the decoration layers and structure tailoring to optimize the energy density versus power density.
- 6. Design of hierarchical and 3D architectures built with a wide range of materials with tailored pore size and morphology. They can support nanoparticles or organic compounds capable of storing multiple electrons per formula unit, thus offering the potential for dramatic increases in energy density.
- 7. Novel nanostructured polymers for batteries and pseudocapacitors that can offer purely organic, printable, flexible, and wearable energy storage solutions.
- 8. Newly discovered materials, such as MXenes, or nanomaterials that have recently found applications in energy storage.
- 9. Nanomaterials that enable the use of multivalent ions, such as Mg²⁺ and Al³⁺, which show much slower diffusion compared to the currently used Li⁺. Those batteries need nanostructured hosts with shorter diffusion paths compared to currently used electrode materials.
- 10. New battery chemistries that require the use of nanoscale processes or materials.

The research topics listed above are important; they can and must be addressed at the nanoscale, and they are more appropriate for ACS Nano than electrochemistry or general materials science/chemistry journals. We are also happy to consider other papers that provide in-depth descriptions of new chemistry, new materials, and/or new electrical energy storage concepts, and those that expand our understanding of the fundamental nanoscale processes that govern energy storage.

Announcements. We are pleased to see that ACS Nano authors Thomas Ebbesen, Stefan Hell, and Sir John Pendry were named as the 2014 Kavli Prize Laureates in Nanoscience.¹¹ Look for a Nano Focus article discussing their work in an upcoming issue.

Disclosure: Views expressed in this editorial are those of the author and not necessarily the views of the ACS.

Yury Gogotsi Associate Editor

REFERENCES AND NOTES

- 1. Yoon, Y.; Lee, K.; Kwon, S.; Seo, S.; Yoo, H.; Kim, S.; Shin, Y.; Park, Y.; Kim, D.; Choi, J.-Y.; et al. Vertical Alignments of Graphene Sheets Spatially and Densely Piled for Fast Ion Diffusion in Compact Supercapacitors. ACS Nano 2014, 8, 4580-4590.
- 2. Farbod, B.; Cui, K.; Kalisvaart, W. P.; Kupsta, M.; Zahiri, B.; Kohandehghan, A.; Memarzadeh Lotfabad, E.; Li, Z.; Luber, E. J.; Mitlin, D. Anodes for Sodium Ion Batteries Based on Tin-Germanium-Antimony Alloys. ACS Nano 2014, 8, 4415-4429.
- 3. Naguib, M.; Mashtalir, O.; Carle, J.; Presser, V.; Lu, J.; Hultman, L.; Gogotsi, Y.; Barsoum, M. W. Two-Dimensional Transition Metal Carbides. ACS Nano 2012, 6, 1322-1331.
- 4. Conway, B. E. Electrochemical Supercapacitors, Scientific Fundamentals and Technological Applications; Kluwer: Dordrecht, The Netherlands, 1999.
- 5. Simon, P.; Gogotsi, Y.; Dunn, B. Where Do Batteries End and Supercapacitors Begin? Science 2014, 343, 1210-1211.
- 6. Augustyn, V.; Come, J.; Lowe, M. A.; Kim, J. W.; Taberna, P.-L.; Tolbert, S. H.; Abruña, H. D.; Simon, P.; Dunn, B. High-Rate Electrochemical Energy Storage through Li⁺ Intercalation Pseudocapacitance. *Nat.* Mater. 2013, 12, 518-522.
- 7. Lv, R.; Cruz-Silva, E.; Terrones, M. Building Complex Hybrid Carbon Architectures by Covalent Interconnections: Graphene-Nanotube Hybrids and More. ACS Nano 2014, 8, 4061-4069.
- 8. Gogotsi, Y. Not Just Graphene. Mater. Today 2012, 15, 574.
- 9. Buglione, L.; Pumera, M. Graphene/Carbon Nanotube Composites Not Exhibiting Synergic Effect for Supercapacitors: The Resulting Capacitance Being Average of Capacitance of Individual Components. Electrochem. Commun. 2012, 157, 45-47.
- 10. Gogotsi, Y.; Simon, P. True Performance Metrics in Electrochemical Energy Storage. Science 2011, 334, 917-918.
- 11. http://www.kavliprize.no/seksjon/vis.html?tid=61429. Accessed June 11, 2014.