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Where Do Batteries End and Supercapacitors Begin?

Patrice Simon,¹ Yury Gogotsi,² Bruce Dunn,³

Batteries keep our devices working throughout the day—that is, they have a high energy density—but they can take hours to recharge when they run down. For rapid power delivery and recharging (i.e., high power density), electrochemical capacitors known as supercapacitors (1) are used. One such application is regenerative braking, used to recover power in cars and electric mass transit vehicles that would otherwise lose braking energy as heat. However, supercapacitors have low energy density.

Batteries and supercapacitors both rely on electrochemical processes, although separate electrochemical mechanisms determine their relative energy and power density. Dur-

ing the past 5 to 7 years, the energy storage field has witnessed a dramatic expansion in research directed at materials that might combine the high energy density of batteries with the long cycle life and short charging times of supercapacitors (2). However, the blurring of these two electrochemical approaches can cause confusion and may lead to unwarranted claims unless careful attention is paid to fundamental performance characteristics.

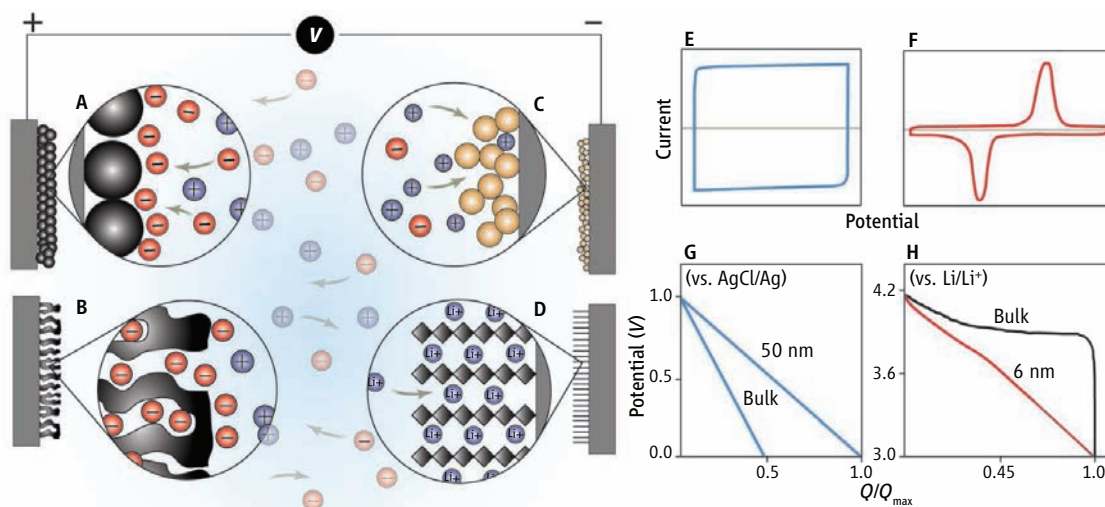
The electrochemical processes occurring in batteries and supercapacitors give rise to their different charge-storage properties. In lithium ion (Li^+) batteries, the insertion of Li^+ that enables redox reactions in bulk electrode materials is diffusion-controlled and can be slow. Supercapacitor devices, also known as electrical double-layer capacitors (EDLCs), store charge by adsorption of electrolyte ions onto the surface of electrode materials (see the figure, panels A to D). No redox reactions are required, so the response to changes in potential without diffusion limitations is rapid and leads to high power. However, the charge

Electrochemical measurements can distinguish between different types of energy storage materials and their underlying mechanisms.

is confined to the surface, so the energy density of EDLCs is less than that of batteries (3). As shown in the figure, panels E to H, supercapacitors can be distinguished from batteries by both potentiostatic and galvanostatic methods. The different methods for achieving double-layer capacitance are characterized by classic rectangular cyclic voltammograms (panel E) and a linear time-dependent change in potential at a constant current (panel G). In batteries, the cyclic voltammograms are characterized by faradaic redox peaks, often with rather large voltage separation (greater than 0.1 to 0.2 V) between oxidation and reduction because of phase transitions (panel F) (4). The presence of two phases is indicated by the voltage plateau in galvanostatic experiments (panel H).

In the 1970s, Conway and others recognized that reversible redox reactions occurring at or near the surface of an appropriate electrode material lead to EDLC-like electrochemical features but the redox processes lead to much greater charge storage

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Comparing batteries and supercapacitors. (A to D) The different mechanisms of capacitive energy storage are illustrated. Double-layer capacitance develops at electrodes comprising (A) carbon particles or (B) porous carbon. The double layer shown here arises from adsorption of negative ions from the electrolyte on the positively charged electrode. Pseudocapacitive mechanisms include (C) redox pseudocapacitance, as occurs in hydrous RuO_2 , and (D) intercalation pseudocapacitance, where Li^+ ions are inserted into the host material. (E to H) Electrochemical characteristics distinguish capacitor and battery materials. Cyclic voltammograms distinguish a capacitor material where the response to a linear change in potential is a constant current (E), as compared to a battery material, which exhibits faradaic redox peaks (F). Galvanostatic discharge behavior (where Q is charge) for a MnO_2 pseudocapacitor is linear for both bulk and nanoscale material (G) (13, 14), but a LiCoO_2 nanoscale material exhibits a linear response while the bulk material shows a voltage plateau (H) (8).

(5). This pseudocapacitance represents a second mechanism for capacitive energy storage. The most widely known pseudocapacitors are RuO_2 and MnO_2 ; recently this list has expanded to other oxides, as well as nitrides and carbides, as different pseudocapacitance mechanisms have been identified (6). Pseudocapacitive materials hold the promise of achieving battery-level energy density combined with the cycle life and power density of EDLCs. To avoid further confusion with EDLCs, we propose that these materials be called oxide supercapacitors (nitride, carbide, etc.) to recognize that a substantial fraction of the charge storage arises from redox reactions. The use of this terminology requires identifying the charge storage mechanism, rather than basing the claim on the material type alone.

A second feature that blurs the distinction between batteries and supercapacitors is how their response changes when nanoscale materials are used. When battery materials are prepared in nanoscale forms, their power density increases because of the short transport paths for ions and electrons (7). However, increased power density does not necessarily transform nanoscale materials into oxide supercapacitors because their faradaic redox peaks and galvanostatic profiles remain battery-like (see the figure, panels F and H). At smaller dimensions (<10 nm), there are indications that traditional battery materials exhibit capacitor-like properties [e.g., LiCoO_2 shown in panel H of the figure (8); V_2O_5 may behave

in a similar fashion (9)]. “Extrinsic” pseudocapacitance can emerge when a battery material is engineered at the nanoscale so that a large fraction of Li^+ storage sites are on the surface or near-surface region.

Pronounced redox peaks in the voltammetry can be an indication of pseudocapacitance, provided the peak voltage differences are small and remain so with increasing sweep rate (5). The kinetic information obtained from sweep voltammetry can also be used. For a redox reaction limited by semi-infinite diffusion, the peak current i varies as $v^{1/2}$; for a capacitive process, it varies as v . This relation is expressed as $i = av^b$ (10), with the value of b providing insight regarding the charge storage mechanism. Over a wide range of sweep rates v , the well-known battery material LiFePO_4 has $b \approx 0.5$, whereas $b \approx 1.0$ for the pseudocapacitor material Nb_2O_5 (6, 11). In addition to diffusion-controlled behavior, low Coulombic efficiency and sluggish kinetics are indications that the material is not a supercapacitor. Thus, an electrode material or a device with well-separated redox peaks (panel F) and a discharge curve similar to the upper curve in panel H should not be considered a supercapacitor.

There is nothing inappropriate in using nanostructured battery materials in symmetric electrochemical cells or combined with a capacitive electrode (carbon) to make a hybrid energy storage device. However, it is misleading to test such a material or device at a low rate (for a supercapacitor, at least

and claim that it is a “high-energy density supercapacitor.” Additionally, the use of low weight loadings or thin films of nanostructured battery materials leads to devices with moderate performance and limited cycle life (12). If the materials are to be considered for high-power devices, they need to be evaluated at the rates where supercapacitor devices are used (e.g., fully recharged in 1 min, referred to as a rate of 60C).

The prospect of developing materials with the energy density of batteries and the power density and cycle life of supercapacitors is an exciting direction that has yet to be realized. Whether to approach these goals by increasing the

power density of battery materials or increasing the energy density of supercapacitors is one of the enticing features of the field. However, there needs to be clarity in the terminology used in combination with appropriate measurements and analyses. Proper evaluation of new materials and their charge storage mechanisms will facilitate progress in this important field of electrical energy storage.

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