# True Performance Metrics in Electrochemical Energy Storage

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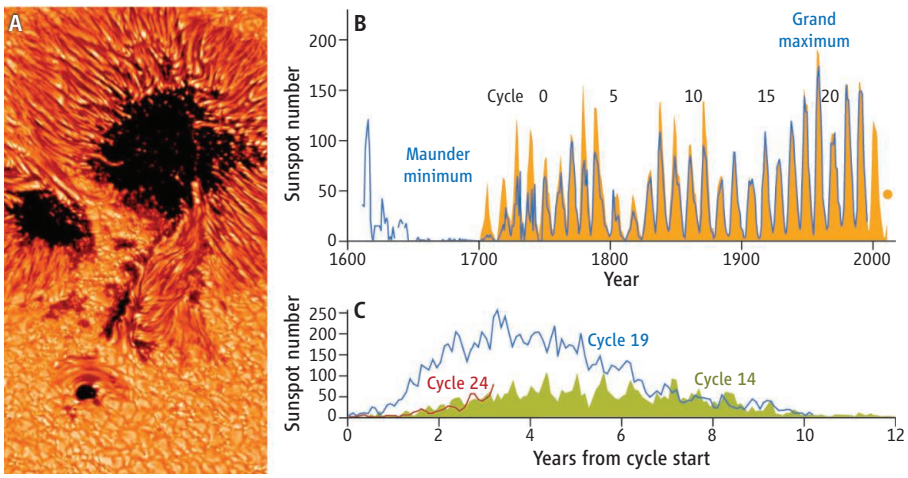


**Solar (in)activity.** (**A**) High-resolution image of a sunspot. (**B**) Yearly averaged Zurich (orange) and group (blue) sunspot number (*4*, *10*, *11*). Before around 1880, group sunspot number is thought to be a more robust representation of actual levels of activity. The Zurich number (also called the Wolf number) was introduced in the 1840s by Rudolf Wolf as an objective measure of the number of sunspots. The group sunspot number is a latter-day improvement, but is not yet officially available for cycle 23. The solid orange circle marks the average over the first 9 months of 2011. (**C**) Monthly averaged Zurich sunspot number for cycles 14 (green), 19 (blue), and 24 (red). Cycle 19 is the strongest on record.

imum starting within the next two decades.

A statistical analysis of earlier grand maxima and minima may provide a bigger-picture view of longer-term behavior of solar activity. As these occurred well before the invention of the telescope, we rely on indirect indicators such as the cosmogenic isotopes $^{14}C$ and $^{10}Be$, produced when cosmic ray particles collide with constituents of our atmosphere. Modeling allows solar activity to be reconstructed back to the beginning of the Holocene period, about 11,000 years ago. The records reconstructed in this manner (*5*–*7*) reveal a rich array of grand minima and maxima. A statistical analysis of the grand maxima shows that they were in general shorter than the one that just ended (*5*, *6*, *8*). Its demise was (statistically) overdue.

What happens after a grand maximum is over? $^{10}Be$ data indicate that the probability of a grand minimum occurring within 40 years of the end of a grand maximum is 8%, rising to 40 to 50% within 200 years (*9*). Similar results are found from the compilation of 27 grand minima and 19 maxima since 9500 B.C.E. based on $^{14}C$ data (*6*). However, there is no guarantee that the Sun will gradually slide into a grand minimum after the just-ended grand maximum. Half the grand maxima in (*6*) were followed by one or more subsequent grand maxima before a grand minimum finally occurred.

In addition, the mean time between the end of a grand maximum and the beginning of the next grand minimum was 318 years. This average interval is also only slightly shorter than the 349 years that passed on average between the end of a grand minimum and the start of the next one. The Maunder minimum ended approximately 300 years ago, which is longer than the majority of such intervals (the median time between grand minima is 240 years), but still short relative to the 1420 years that passed between the two grand minima that occurred between 3000 and 5000 years ago.

Prediction of solar activity has not been reliable, because of the nonlinearity of the solar dynamo producing the magnetic field that is responsible for solar activity. On long time scales, our best bet is to consider the statistical evidence gleaned from previous grand minima and maxima. But these also give a mixed message. A grand minimum might be just around the corner and could hit us in the next 30 years, although with a probability below 10%. It is not even clear in which direction solar activity will develop in the longer term. Thus, the next grand extremum is just as likely to be a maximum as a minimum.


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MATERIALS SCIENCE

# True Performance Metrics in Electrochemical Energy Storage


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Exceptional performance claims for electrodes used in batteries and electrochemical capacitors often fail to hold up when all device components are included.


A dramatic expansion of research in the area of electrochemical energy storage (EES) during the past decade has been driven by the demand for EES in handheld electronic devices, transportation, and storage of renewable energy for the power grid (*1*–*3*). However, the outstanding properties reported for new electrode materials may not necessarily be applicable to performance of electrochemical capacitors (ECs). These devices, also called supercapacitors or ultracapacitors (*4*), store charge with ions from solution at charged porous electrodes. Unlike batteries, which store large amounts of energy but deliver it slowly, ECs can deliver energy faster (develop high power), but only for a short time. However, recent work has claimed energy densities for ECs approaching (*5*) or even exceeding that of batteries. We show that even when some metrics seem to support these claims, actual device performance may be rather mediocre. We will focus here


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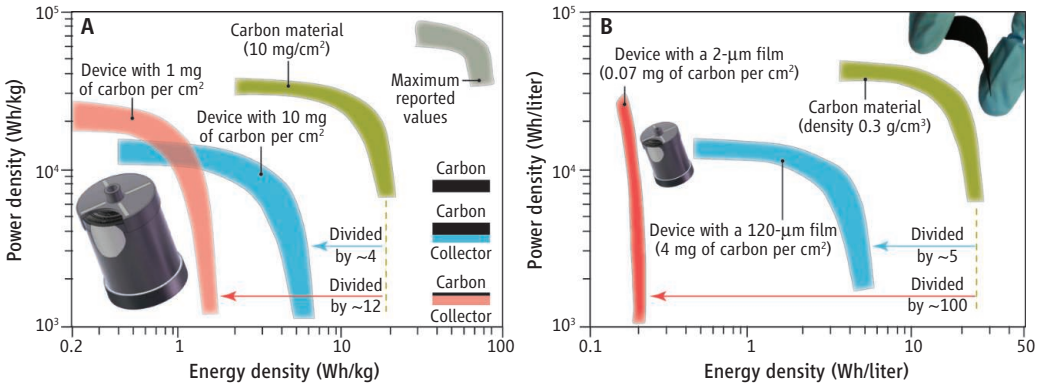


**A tale of two plots**. One way to compare electrical energy storage devices is to use Ragone plots (*10*), which show both power density (speed of charge and discharge) and energy density (storage capacity). These plots for the same electrochemical capacitors are on a gravimetric (per weight) basis in (**A**) and on a volumetric basis in (**B**). The plots show that excellent properties of carbon materials will not translate to medium- and large-scale devices if thin-film and/or low-density electrodes are used (*10*).

on ECs, but these considerations also apply to lithium (Li)–ion batteries.

Typically, the performance of both batteries and ECs is presented by using Ragone plots (see the figure) that show the relation between energy density (how far an electric car can go on a single charge) and power density (how fast the car can go). A commercial EC can harvest or release more energy than a typical Li-ion battery can deliver on time frames of less than 10 s, and it can be used for an almost unlimited number of charge and discharge cycles (*4*). A near-term application will be storing energy for car starter motors to allow engine shut-offs when stopped (*6*) and harvesting braking energy.

Increasing the energy density of ECs usually comes at the cost of losses in cyclability (*5*) or power, which are the most important properties of ECs and without which they become mediocre batteries. A major effort has been directed toward increasing the energy density of ECs by either increasing the capacitance of the material, $C$, or the operation voltage window, $V$, or both, since the energy stored is proportional to $CV^2$. Some recent publications on graphene and nanotube-based materials have used Ragone plots to argue that supercapacitors can achieve the energy density of batteries. Those claims are summarized in the gray area in the upper right corner of panel A in the figure.

Reporting the energy and power densities per weight of active material alone on a Ragone plot (panel A) may not give a realistic picture of the performance that the assembled device could reach because the weight of the other device components also needs to be taken into account. ECs are similar to Li-ion batteries in that they contain current collectors, electrolyte, separator, binder, connectors, and packaging, in addition to carbon-based electrodes. Because the carbon weight accounts for about 30% of the total mass of the packaged commercial EC, a factor of 3 to 4 is frequently used to extrapolate the energy or power of the device from the performance of the material. Thus, the energy density of 20 Wh/kg of carbon will translate to about 5 Wh/kg of packaged cell.

However, this extrapolation is only valid for electrodes with thicknesses and densities similar to those of commercial electrodes (100 to 200 μm or about 10 mg/cm² of carbon film). An electrode of the same carbon material that is 10 times thinner or lighter will reduce energy density by three- to fourfold (from 5 down to 1.5 Wh/kg based on cell weight, see panel A), with only a slight increase in power density. Our ability to predict the performance of a 200-μm-thick electrode by testing a 1-μm film (*7*) or a small amount of material in a cavity microelectrode (*8*) is still very poor. Experimental data show that there may be an additional drop in the capacitance by a factor of 2 to 3 when the thickness of the nanoporous carbon electrode increases (*7*).

Much of this uncertainty stems from reporting gravimetric, rather than volumetric, energy and power densities of materials and devices. Many nanomaterials, such as nanotubes or graphene, have a low packing density (<0.5 g/cm³), which leads to empty space in the electrode that will be flooded by electrolyte, thereby increasing the weight of the device without adding capacitance. An extreme case would be the use of a carbon aerogel with 90% porosity. The volumetric energy of such an electrode will be 20% that of a carbon electrode with just 50% porosity.

If we consider a low-density graphene electrode (0.3 g/cm³) with an extremely high gravimetric energy density of 85 Wh/kg (gray area in panel A of the figure), its volumetric density will be 25.5 Wh/liter for the electrode and ~5 Wh/liter for the device (panel B), which is a typical value for commercial ECs with activated carbon. If a 2-μm film of the same material is used in the device, a much greater drop occurs, which is why "paper batteries" or thin-film ECs cannot be used for storing large amounts of energy.

The gravimetric energy density is almost irrelevant compared to areal or volumetric energy for microdevices and thin-film ECs, because the weight of the active material used in a micrometer-thin film on a chip or a nanotube coating on a smart fabric is negligible. These systems may show a very high gravimetric power density and discharge rates, but those characteristics will not scale up linearly with the thickness of the electrode (*7*), i.e., the devices cannot be scaled up to power an electric car. Ragone plots are only one measure of a device; they do not show other important properties, such as the device's cycle lifetime, energy efficiency, self-discharge, temperature range of operation, or cost. They may also provide misleading information for flow and semisolid batteries (*3*, *9*), where energy and power densities are decoupled.

By presenting energy and power densities in a consistent manner, we can facilitate introduction of new materials and find solutions for EES challenges the world faces. National and international testing facilities should be created for benchmarking electrodes and devices similar to the facilities that exist for benchmarking photovoltaics. Clear rules for reporting the performance of new materials for EES devices would help scientists who are not experts in the field, as well as engineers, investors, and the general public, who rely on the data published by the scientists, to assess competing claims.


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10. Details for the figure plots are available at *Science* Online.


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**Supporting Online Material**

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