A capacity for change

Materials issues in supercapacitor technology

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Owners of a Toyota Prius have a right to feel smug. With fuel consumption of up to 53 miles per gallon, the latest Prius c model is rated as the most fuel-efficient compact hybrid car on the market. It's tempting to attribute that performance to the vehicle's nickel-metal hydride batteries, but a big part of the credit must also go to the 20 or so little cells that supply spurts of power for controlling auxiliary functions such as the electric windows and heating. These clever devices, called supercapacitors (SCs), also capture some of the kinetic energy released during braking, storing it electrically and then releasing it when needed, for example to restart the engine when it switches off as the car idles at a red light. Batteries can't do that.

Energy-storing SCs are becoming ubiquitous in electrical and hybrid transportation, particularly in public trains, trams and buses. Shanghai now has an extensive public bus network that uses SCs in regenerative braking to lower fuel consumption, and they are also found in buses and trams in France, Germany, Italy and the UK. Other car companies, such as Citroën, Peugeot and Mazda, are using them in hybrids, and they were even incorporated into Toyota's TS030 racing car for the 2012 speed race at Le Mans. In diesel buses and trucks, SC-based regenerative braking can cut fuel costs by around 30 percent annually, with a corresponding reduction in carbon-dioxide emissions.

They are ideally suited to 'start-stop' hybrid vehicles that temporarily shut down the internal combustion engine while at a standstill – buses at passenger stops, say, and garbage trucks picking up and setting down. Whereas batteries take hours to charge, SCs need only a few seconds, so buses can recharge in the short wait at stops. Such rapid recharging is envisaged for SCs helping to power electric shuttle boats planned for the French port of Marseilles.

Because they supply short (up to 30-second) bursts of energy, supercapacitors are also well suited to applications such as cordless power tools and heavy-construction machinery. They are used as power sources on satellites and other space technology, and in aerospace engineering. "In the mid-2000s, the use of supercapacitors for opening doors of the A380 Jumbo jet was the first demonstration of the maturity of the technology", says Patrice Simon, a materials scientist at the Université Paul Sabatier in Toulouse, France. "It was a niche market, but the impact has been really important in supercap development" – because it showed that these devices could perform safely and reliably in a demanding situation where those factors were paramount.

Among the principal producers of supercapacitors today are the California-based Maxwell Energy, which supplies them to the Prius, and the Korean firm Nesscap. As the market grows, however, small manufacturers are springing up that promise new types of SC that exploit innovations in materials technology and new designs. But SCs are still relatively expensive, partly because the limited demand for them means they have not been able to benefit from economies of large-scale production. The market could expand substantially if the performance of SCs – in particular their energy and power densities – can be improved. That will depend on clever materials engineering.[1]

Power surge

Supercapacitors are occasionally depicted as competitors to batteries as devices for storing and delivering energy. But at face value they don't compete very well: state-of-the-art SCs have energy densities (energy capacity per unit mass) of around 4-5 watt-hours per kg, whereas lithium-ion batteries achieve over 120 Wh kg^{-1}. This isn't surprising: batteries store energy in the bulk of their materials, while supercapacitors do so only at the electrode surfaces. "Bearing in mind the difference in nature in the storage mechanism, it seems impossible currently to bring the energy density of SCs close to that of batteries", says Simon.

But that's not really the point. Whereas batteries charge and discharge through slowly unfolding electrochemical reactions, SCs can grab and dump all their stored charge in an instant. They are therefore ideal in applications where energy needs to be captured and released quickly – in other words, where the key requirement is not so much high energy as high power. "The main markets are wherever one needs to deliver current bursts or to consume current surges", explains Donald Sadoway, a materials chemist at the Massachusetts Institute of Technology. Improving the energy density is worthwhile, but only if it doesn't compromise the very high power density and long lifetimes that make SCs attractive for their current uses. And rather than seeing them as alternatives to batteries, they are more usefully viewed as complementary: SCs to manage current bursts, batteries to supply the stamina. "On a car, for example, the SC can handle the current surges that arise from electromagnetic braking and the subsequent current burst needed for acceleration", says Sadoway, "while the battery can provide more modest current for long periods to achieve distance."

Supercapacitors were first developed in the 1950s, and commercialization began in the 1970s. Like familiar electrical capacitors, they store energy by charging up electrodes and then release it during discharge. But they are 'super' because they store so much more energy than conventional capacitors – and they do this by accumulating charge not as electrons *on* the conducting electrodes but as ions adsorbed from an electrolyte into pores *within* the electrodes.

Whereas in an ordinary capacitor the electrodes are simply conductive plates separated by an insulating dielectric material, SCs have a different structure. The most common type of device, an electrical-double-layer (EDL) supercapacitor, consists of two porous electrodes, usually made of activated carbon (deposited on aluminum foil), saturated with an electrolyte and separated by a thin polymer membrane. For the electrolyte, current commercial devices generally use organic salts such as $[N(C_2H_5)_4]^+BF_4^-$ in an organic solvent such as acetonitrile or propylene carbonate. During charging, the potential applied to the porous electrodes draws ions from solution onto their surface. A layer of counterions then accumulates right next to the ion-coated electrodes, creating a so-called electrical double layer. It is the intimate proximity of charge separation in this double layer that provides the capacitance: the smaller the separation of charge, the greater the capacitance. When the device is discharged, the ions return to the electrolyte.

The capacitance can be further enhanced by making use of battery-like electrochemical processes: redox reactions that are fast enough to sustain the rapid charge-discharge behavior. Such devices are called pseudocapacitors. Their electrodes are not carbon but substances that may undergo redox processes, typically transition-metal oxides such as RuO_2, Fe_3O_4, MnO_2 and TiO_2 deposited as thin films on porous supports such as carbon or fashioned into nanorods, tubes or other nanostructures. Some pseudocapacitors use electrically conducting polymers such as polyaniline. Typical reactions involve the protonation of the metal oxides or the intercalation of metal ions in the electrolyte, such as lithium and sodium. However, the redox reactions tend to result in a decline in performance over many charge-discharge cycles.

Thierry Brousse of the University of Nantes in France, president of the evaluation committee for the French National Research Agency PROGELEC program on energy storage, says that the key aims for improving electrochemical capacitors are to achieve higher energy density while retaining high power density and long lifetime (more than 100,000 cycles), to improve safety, and to achieve coupling with other devices, such as batteries and photovoltaics. “Optimizing today's products means finding better carbon electrodes and electrolytes”, says Brousse. “New devices definitely need new materials.”

New wrinkles in carbon

The most obvious way to increase the energy density of SCs is to increase the surface area of their electrodes, packing in more ions during the charging cycle. “The key desirable electrode characteristics for carbon systems are a high surface area together with a controlled pore size in the microporous range”, says Simon. The electrode materials must also be thermally stable and resistant to corrosion. The advent of nanostructured forms of carbon over the past two decades has attracted great interest from researchers looking to boost SC surface area.[2] Forests of aligned carbon nanotubes are being explored by several groups for SCs, and the start-up company FastCap, a spinoff from research at the Massachusetts Institute of Technology, aims to commercialize them. FastCap has made prototype devices with nanotube electrodes that achieve energy densities of 20-25 Wh kg^{-1} – still a way off lithium batteries, but comparable to lead-acid batteries. But producing high-quality films of aligned carbon nanotubes is still challenging and expensive.

Another potential source of high-area carbon electrodes is graphene: sheets of graphite-like carbon just one atom thick. In 2008 Rodney Ruoff at the University of Texas at Austin and coworkers reported graphene-based SCs prepared from individual layers of graphite oxide, an oxidized form of graphite that can be separated into individual layers relatively easily because of its solubility in water.[3] When they chemically reduced suspensions of the graphite oxide sheets back to graphene, the sheets agglomerated into microparticles from which crumpled sheets extend into the solution, offering a high surface area. The researchers showed that these particles could be used in SC electrodes in aqueous and non-aqueous solvents. And last year Ruoff's team reported SCs made from graphite oxide exfoliated using heat or microwaves and then treated with an alkali to form graphene sheets interconnected into a three-dimensional network of pores 1-10 nm wide, with a very high surface area.[4] They used this material to make SCs with an energy density comparable to the FastCap nanotube cells, and with a storage capacity that barely declines after 10,000 charge-discharge cycles. Ruoff's work has spawned a company called Graphene Energy, based in Austin. Another company, Nanotek Instruments in Dayton, Ohio, has also developed a method for making curved graphene sheets that, because of their shape, cannot simply stack into layers and so will crumple into a high-surface-area form.[5] They claim that electrodes made from this stuff could provide SCs with energy densities of around 28 Wh kg^{-1}.

That by no means exhausts the possibilities for nanostructured carbon. Simon and colleagues have made tiny SCs just a few micrometres across with electrodes fabricated from carbon 'onions' – curved graphene-like shells in a concentric arrangement, 6-7 nm wide, deposited onto a surface.[6] "Graphene, carbon nanotubes and carbon onions are very promising candidates for micro-devices thanks to their high capacitance when processed into thin films a few tens or hundreds of nanometres thick", says Simon. Such devices could open the door to new applications of SCs, for example as power sources in portable electronics and in medical implants used for drug delivery, which could be triggered by pulses of electricity. A group at Rice University in Houston, Texas, has demonstrated that microscale SCs can be made from graphite oxide films by using lasers to reduce the material locally and 'write in' microscopic graphene electrodes. The remaining graphite oxide intervening between the electrodes can act as a solid electrolyte for the devices.[7] Simon says that for these carbon-based materials it is essential to keep the surfaces as free as possible from functional groups, which are vulnerable to chemical attack and so can lead to rapid ageing.

Some researchers are using new forms of nanostructured carbon as supports for manganese oxide (MnO_2) in pseudocapacitors. MnO_2 is relatively cheap and non-toxic and is already used in lithium-ion batteries. It is a poor conductor, but that problem can be overcome by using it as ultrathin films or very small particles. For example, using MnO_2 nanoparticles embedded in the walls of an ordered nanoporous form of carbon called CMK3 formed on a template of porous silica, Jianlin Shi and colleagues at the Shanghai Institute of Ceramics have made pseudocapacitors with high capacitance.[8] Such devices could work well with aqueous electrolytes, both keeping costs down and improving the device safety. "People try to avoid using acetonitrile" says Brousse. He and his coworkers have been exploring the use of aqueous sodium sulphate and lithium nitrate in electrochemical capacitors with carbon/MnO_2 electrodes.[9]

Another promising avenue to nano-carbon electrodes is a method developed by Yury Gogotsi of Drexel University in Philadelphia and coworkers, in which they extract the metals from metal carbides by chemical etching with chlorine to leave behind pure carbon material, which they call carbide-derived carbon (CDC).[10] The process can generate almost all the known forms of nano-carbon, such as ‘nano-ribbons’ of graphite, aligned carbon nanotubes and carbon onions, as well as amorphous, nanoporous carbon with very high surface area and precisely defined and tunable pore size. The Estonian company Skeleton Technologies uses this procedure to make SCs with energy densities of up to 6.9 Wh kg^{-1}, the highest so far for a commercial device.[11]

New designs

Quite aside from these materials innovations, some researchers think that the performance of SCs can be boosted by entirely new designs. One such, developed by Gogotsi in collaboration with Emin Kumbur at Drexel, is a device called the electrochemical flow capacitor, a cross between a SC and a kind of battery.[12] Here the storage capacity is made very large by locating the charge not in some porous medium at the electrode but in a slurry of porous carbon microspheres, each a couple of hundred micrometres across, which pick up ions as they flow past the electrodes en route from one reservoir to another. They return the ions when pumped back during discharge. The Drexel team claims that the device should last for around 100,000 or more charge-discharge cycles.

Another option is to fully integrate battery-like behaviour with capacitive, to exploit the best of both worlds: high power and energy densities. Such cells might combine a graphite electrode like those in lithium batteries, which intercalates lithium ions, with a capacitive carbon material. This approach is being pursued by Aquion Energy, a spin-off company from research led by materials scientist Jay Whitacre of Carnegie Mellon University in Pittsburgh. Whitacre and colleagues have developed a hybrid which works as an EDL cell, a pseudocapacitor and a lithium battery.[13] It contains a porous activated-carbon anode with pseudocapacitor behavior, and a layered manganese oxide cathode in which sodium and lithium ions can be intercalated. The electrolyte is aqueous sodium sulphate, but it picks up some lithium too, lodged in the cathode during synthesis and gets released in the first charging cycle. “It’s much more of an energy-storage device”, Whitacre explains, “with a low power density but charge and discharge events over many hours” – really more of a battery than a supercapacitor, with a voltage of up to 1.9 V. The key to commercial viability, says Whitacre, is to use cheap materials and established (‘borrowed’) manufacturing methods: for the activated carbon anode, the team forsakes expensive materials developed for SCs in favour of a material made by pyrolysis of caramelised glucose. Aquion has begun working on a plant near Pittsburgh that should start producing the batteries in 2013.

A supercap-battery hybrid called the Ultimo is also being developed by the Japanese company JM Energy, and Nesscap is also working on them too. These devices have voltages of up to 4 V and energy densities approaching those of batteries: around 15 Wh kg^{-1}, three times what is possible with conventional EDL supercapacitors. They are, in contrast to Aquion’s cells, more supercap than battery. “They use organic solvents and are made to support higher power pulses”, says Whitacre, “while we’re focusing on low-power, long-duration, high-energy applications. Our devices are less expensive and contain no toxic or flammable materials.”

A potential difference

The voltages of conventional SCs are typically restricted to less than 3 V. This is a nuisance in some applications – vehicle electrics, for example, usually work at 24 V, requiring the use of several of these costly cells in series. What's more, the low voltages limit the energy and power performance. "Both the energy and the power density are proportional to the voltage squared", explains Simon, "so increasing the cell voltage is a key concern."

But higher voltages decompose the commonly used electrolytes. A promising solution is to replace them with ionic liquids: ionic materials that are liquid at room temperature, which are typically very thermally stable as well as being extremely non-volatile. Supercapacitors using a eutectic (low-melting-point) mixture of ionic liquids can operate over a very wide temperature range of -50 to 100 ^{o}C.[14] Some commercial SCs already use these solvents to achieve voltages of 3 V, but they could in principle go up to 4-5 V. They still have drawbacks, however. One is their limited ionic conductivity at room temperature; Sadoway also points out that many of the commonly used ionic liquids are also themselves somewhat unstable at high voltages, since the cations tend to undergo redox reactions. He has been working on new cations that don't suffer from this problem.

It's likely that the most effective electrolytes will be tailored for compatibility with the electrode material. For example, Ruoff and colleagues have found that one particular polymeric ionic liquid, with imidazolium groups attached to a hydrocarbon backbone, will form complexes with residual oxygen-bearing groups on reduced graphene oxide, both stabilizing them and helping other ionic liquids to access the electrode surface. In this way he and his colleagues have made ionic-liquid supercapacitors with respectable energy densities of 6.5 Wh kg^{-1} and operating voltages of up to 3.5 V.[15] "We have tried adapting the carbon porous structure to the electrolyte used", says Simon, who has reported cell voltages up to 3.7 V for ionic liquids with nanostructured carbon electrodes. "How to computationally select and optimise an electrode/electrolyte couple is one of the key future questions for supercapacitors", says Gogotsi.

For the future

There are several other open questions too. Despite all the recent progress, some aspects of the fundamental science of supercapacitors are still not well understood. One is the question of how ions behave at the interfaces of the porous electrodes. It was widely believed, for example, that the surface area accessible to the ions was limited by the pore size: ions would not be able to penetrate into pores narrower than about 1 nm, because this is smaller than the diameter of the ion's solvation shell, the cloud of solvent molecules that surrounds it. But experiments by Gogotsi, Simon and their coworkers using porous CDC films with pore sizes of 0.6-2.25 nm have shown that in fact ions can still get inside the narrowest pores, producing exceptionally high capacitance.[16] In fact their capacitance shoots up, rather than declining, at pore diameters of around 1 nm, which the researchers tentatively attribute to a distortion of the tightly squeezed solvation shell that allowed the ions to approach even more closely to the electrode surface. “This was a real breakthrough that defied the conventional view of ion adsorption”, says Simon. But he adds that “we still need to better understand the desolvation mechanism – and the associate capacitance increase - as well as the reason why the ion transport inside such small pores is so surprisingly fast.” Such studies could have ramifications in other fields too, ranging from biology (for example, the transport of ions through protein ion channels) to water desalination, one approach to which uses carbon nanotubes to filter out ions.

The biggest challenge for making supercapacitors a major force in energy efficiency and green technology, however, is to make them cheaper. “The main obstacle to their wider use is cost”, says Sadoway. “Researchers tend to overlook this and instead focus on the electrical performance metrics. Many scientists are under the impression that if we produce items in large enough quantities, the economies of scale will drive the cost of production down to the price point of the market. With the impeding collapse of A123 Systems [the beleaguered US battery company that supplies General Motors and others with lithium batteries for vehicles] we have a vivid example of how faulty this line of thinking is.”

While bigger, more powerful and capacious SCs would boost their heavy-duty use in industry and transport, new designs and approaches would open up entirely new niches. “Flexible systems, where the electrodes and the electrolyte are deposited onto flexible current collectors, are getting growing attention”, says Simon. Microscale cells will find uses in microelectronic and medicine, while small and versatile devices could also find applications in smart textiles for military and fashion markets. In just a few years, you never know where these power packs might turn up.

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