

Batteries and electrochemical capacitors

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Present and future applications of electrical energy storage devices are stimulating research into innovative new materials and novel architectures.

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Electricity generated from renewable sources, such as solar and wind power, offers enormous potential for meeting future energy demands. But access to solar and wind energy is intermittent, whereas electricity must be reliably available for 24 hours a day: Even second-to-second fluctuations can cause major disruptions that cost tens of billions of dollars annually. Electrical energy storage devices will therefore be critical for effectively leveling the cyclic nature of renewable energy sources. (See the article by George Crabtree and Nathan Lewis, *PHYSICS TODAY*, March 2007, page 37.) They are also a key enabler in numerous areas of technological relevance ranging from transportation to consumer electronics.

Electrical energy storage systems can be divided into two main categories: batteries and electrochemical capacitors. Batteries store energy in the form of chemical reactants, whereas ECs store energy directly as charge. Due to that fundamental difference between the systems, they exhibit different energy and power outputs, charge–discharge cyclability, and reaction time scales.

Batteries can generally store significantly more energy per unit mass than ECs, as shown in figure 1a, because they use electrochemical reactions called faradaic processes. Faradaic processes, which involve the transfer of charge across the interfaces between a battery's electrodes and electrolyte solution, lead to reduction and oxidation, or redox reactions, of species at the interfaces. When a battery is charged or discharged, the redox reactions change the molecular or crystalline structure of the electrode materials, which often affects their stability, so batteries generally must be replaced after several thousand charge–discharge cycles.

On the other hand, ECs show no major changes in the properties of the electrode materials during operation, so they can be charged and discharged up to millions of times. The charge-storing processes employed in ECs are much faster than the faradaic processes in batteries, so although ECs have lower energy densities than batteries, they have higher power densities. Furthermore, their operation time scales are quite different: ECs can be charged and discharged in seconds, whereas high-performance rechargeable batteries require at least tens of minutes to charge and hours or days to discharge. Those differences have made for different market applications and opportunities, depending on the

performance needs. In fact, some important applications require the use of batteries and ECs in combination. For example, the next generation of hybrid vehicles will likely incorporate batteries and ECs.

However, the performance of current energy storage devices falls well short of the requirements for using electrical energy efficiently. Devices with substantially higher energy and power densities, faster recharge rates, and longer charge–discharge cycle lifetimes are needed if plug-in hybrid and pure electric vehicles are to be developed and broadly deployed as replacements for gasoline-powered vehicles. Moreover, the reliability and safety of the devices must be improved to prevent premature and sometimes catastrophic failures.

To meet the future needs of electrical energy storage, it is critical to understand atomic- and molecular-level processes that govern their operation, performance limitations, and failure. Engineering efforts have incrementally advanced the performance of the devices, but breakthroughs are needed that only fundamental research can provide. The goal is to develop novel energy storage systems that incorporate revolutionary new materials and chemical processes.¹

Batteries

A battery is composed of an anode (negative electrode), a cathode (positive electrode), and an electrolyte that allows for ionic conductivity. Rigid separators (made of polymeric materials, for example) separate the anode and cathode to prevent a short circuit. Today commercially available rechargeable batteries include lithium-ion, nickel-metal-hydride, and nickel–cadmium devices. As shown in figure 1b, lithium-ion and other lithium-based batteries have the highest energy densities (per unit volume or per unit mass) of all rechargeable batteries. First commercialized by Sony Corp in 1990, lithium-ion batteries (LIBs) are now used in portable electronic devices, power tools, stationary power supplies, and medical instruments and in military, automotive, and aerospace applications. They are likely to be among the most important energy storage devices of the future.²

Figure 2 depicts the charge and discharge processes for a conventional LIB.³ In the discharge process, the anode is electrochemically oxidized, which results in the release, or

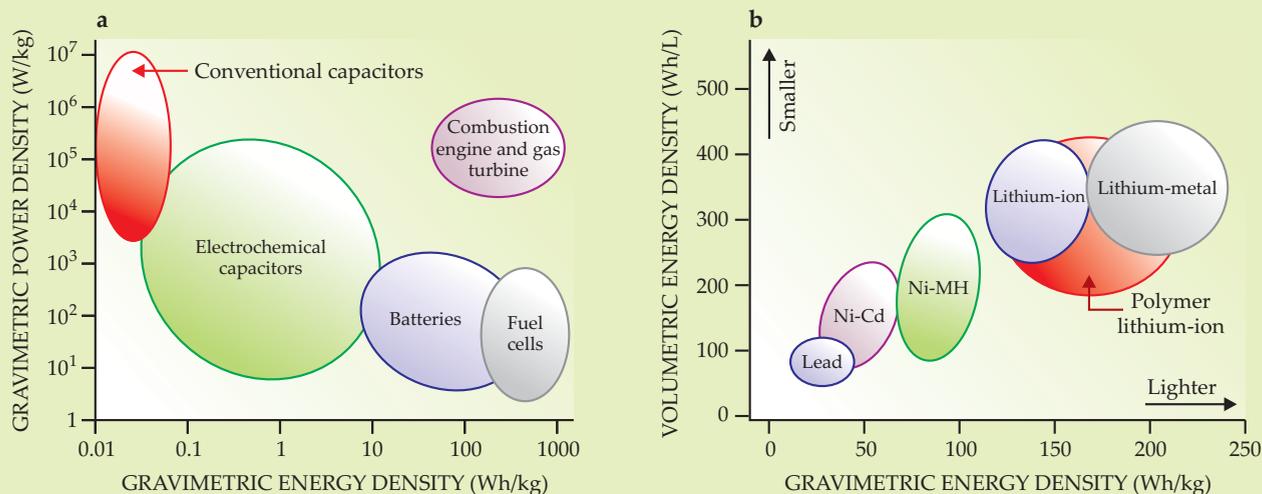


Figure 1. (a) Batteries store more energy per unit weight than electrochemical capacitors, but ECs provide more power. Thus batteries tend to be preferred for long-time operation of a device, whereas ECs are used to provide high power in a short time period. Other systems for generating and storing energy are shown for comparison. **(b)** Rechargeable batteries include those based on lead, nickel–cadmium, and nickel–metal hydride. But lithium-based batteries store the most energy per unit mass or per unit volume.

deintercalation, of Li ions into the electrolyte. At the same time, electrons move through the external circuit and travel toward the cathode. The Li ions travel through the electrolyte to compensate for the negative charge flowing through the external circuit, which results in the uptake, or intercalation, of Li ions into the cathode. When the battery is recharged, the reverse processes occur. In this mode of operation, LIBs are generally called rocking-chair batteries to describe the toggling of Li ions back and forth between anode and cathode.

The energy output of a battery depends on the operating voltage (determined by the redox reactions that take place at the two electrodes) and the charge storage capacities of the electrode materials. However, a battery does not always deliver as much energy as it theoretically can. For example, when a battery is discharged rapidly to provide high power, an overpotential is needed to drive the electrode reactions at sufficiently fast rates, which decreases the operating voltage and therefore the energy. To minimize that energy loss, researchers are interested in identifying reactions that proceed sufficiently fast on their own or that can be suitably catalyzed. Ohmic losses, which result from the electrical resistance of the electrolyte and contact resistances at the electrodes, also lower a battery's energy output.

The high energy outputs of Li-based batteries are mainly a result of the electrochemical and physicochemical properties of Li. As the lightest metal, Li has a theoretical gravimetric capacity—storable charge per unit weight—of 3860 mAh/g. Moreover, Li is the strongest metal reducing agent. A Li anode thus generates a large potential difference between the anode and cathode, which leads to a larger energy output.

However, significant safety issues are associated with the use of Li metal as an anode material. When the current distribution during the charging process is not uniform, Li metal dendrites can form at the anode surface, which can cause short circuits. Anodes of commercially available LIBs are instead typically made of carbonaceous materials such as graphite, which are capable of intercalating one Li atom per six carbon atoms—LiC₆—when the battery is fully charged.⁴

With the aim of enhancing the anode capacity, researchers have focused on materials such as silicon, tin, metal oxides, and Li alloys.⁴ Research is also under way to design safer Li metal anodes by improving the reversibility of Li electro-deposition (thus mitigating dendrite formation) or preventing the deposition altogether.

The cathodes of LIBs are typically made of metal oxides and phosphates.⁵ LiCoO₂ has been used most extensively in practical applications, but cobalt is relatively expensive. The cost and availability of materials is becoming a more important consideration as the market for LIBs grows and targets larger applications, such as hybrid and pure electric vehicles, for which vast amounts of material will be required. Mixed layered oxides (such as LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂) and LiFePO₄ have therefore captured the attention of numerous research groups.⁶ Their electrochemical performance is comparable to that of LiCoO₂, they are less expensive, and they are thermally more stable and therefore safer. In fact, LIBs based on the mixed layered oxide and LiFePO₄ cathodes have been commercialized, respectively, by Sony and A123 Systems Inc.

Capacities obtainable from conventional inorganic cathode materials are limited by the number of lithium ions that they can intercalate while remaining structurally stable. When Li ions are deintercalated from an oxide such as LiCoO₂, the material's lattice contracts. Extraction of all, or even 80–90%, of the Li ions would change the structure so much that the electrode would fail after a small number of charge–discharge cycles. In practice, therefore, batteries are generally designed so that only about half of the Li ions are ever deintercalated from the cathode. The gravimetric capacities of cathode materials are thus limited to 120–160 mAh/g.

Anode materials, in contrast, have gravimetric capacities of 372 mAh/g or more. The capacity difference between anode and cathode materials means that the cathode in an LIB must be several times more massive than the anode. That imbalance affects not only the energy density of the battery as a whole but also its charge–discharge performance. The need for more cathode material means that the cathode will be thicker, so the Li ions must travel a greater distance to undergo intercalation

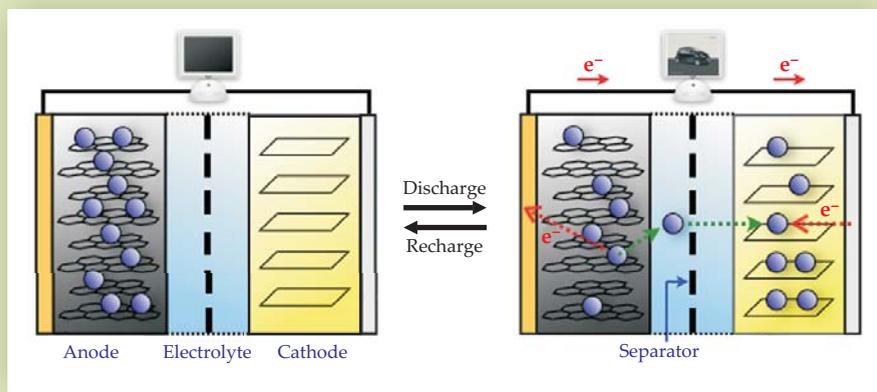


Figure 2. Charging and discharging a lithium-ion battery. In the discharge process, the anode is electrochemically oxidized, and intercalated Li ions (purple) are released. At the same time, electrons travel through the external circuit to the cathode. The Li ions travel through the electrolyte and are intercalated in the cathode. When the battery is recharged, the reverse processes occur.

and deintercalation. It is thus particularly important to develop cathode materials with higher capacities.

Recently, researchers have paid a great deal of attention to organic materials as a feasible solution to increasing cathode capacities. The building blocks of organic compounds—carbon, nitrogen, oxygen, and sulfur—are all abundant and inexpensive. Since organic materials are generally amorphous, the problem of structural changes during charge and discharge is precluded. Moreover, chemical tunability of the compounds makes them even more attractive. Organic materials can be designed to optimize the capacity, energy, or charge–discharge cycle performance, as desired.

Organic molecules containing S, O, or N atoms appear to be especially promising. As cathode materials, they may provide reversible and fast charge-transfer reactions in addition to high gravimetric capacities. In particular, organosulfur compounds with multiple thiolate (S^-) groups have been extensively considered due primarily to their high theoretical gravimetric capacities, as shown in figure 3a.⁷ The charge and discharge reactions are based on formation and cleavage of disulfide bonds, so the number of electrons transferred per unit weight is determined by the number of thiolate groups, which can be made quite large. (However, they offer no significant advantage in terms of volumetric capacity because organic materials are generally less dense than inorganic materials.) In addition, organosulfur compounds can release and capture Li ions during charge and discharge reactions, so they can easily be incorporated into the rocking-chair system.

But the redox reactions of thiolate compounds are generally very slow at room temperature, so efficient electrocatalysts, such as conducting polymers, are required to accelerate the reactions.⁸ Moreover, thiolate compounds often exhibit poor charge–discharge cyclability due to dissolution of the reduction products (the thiolate monomers in figure 3b), particularly when the electrolyte is an organic liquid. In order for organosulfur compounds to be of practical use as high-energy cathode materials, procedures or novel materials must be developed to prevent such dissolution. Elemental sulfur, S_8 , whose charge–discharge reactions likewise involve formation and cleavage of disulfide bonds, has also been widely studied as a cathode material due to its exceptionally high gravimetric capacity. However, similar to organosulfur compounds, issues related to slow kinetics and dissolution of the reduction

products of S_8 have precluded its practical use.

Electrochemical capacitors

Like a conventional capacitor, an electrochemical capacitor stores energy as charge on a pair of electrodes. Unlike a conventional capacitor, however, an EC stores charge in an electric double layer that forms at the interface between an electrode and an electrolyte solution, as shown in figure 4.⁹ The electrolyte can be an aqueous solution such as sulfuric acid or potassium hydroxide, an organic electrolyte such as acetonitrile or propylene carbonate, or an ionic liquid. As in LIBs, gel- and solid-type polymer electrolytes have also been used to improve safety and thus system reliability.

Because of their intrinsically fast mechanism for storing and releasing charge, ECs are well suited for applications that require high power. In particular, they can store energy that is normally wasted as heat during repetitive motions such as the deceleration of automobiles during braking. Light hybrid vehicles have successfully used batteries for that purpose, but heavy vehicles, such as buses and trucks, need more power, so ECs are more suitable. Other applications of ECs include energy management in cranes, forklifts, and elevators.

The charge that can be stored in an EC is proportional to the surface area of the electrodes, so both the anode and the cathode are typically made of activated carbon, a porous material whose internal surface area can exceed 1000 m^2/g . ECs typically have capacitances of 100–140 F/g and energy densities of 2–5 Wh/kg—several orders of magnitude greater than those of conventional capacitors—so they are often called supercapacitors or ultracapacitors.¹⁰

New types of carbon materials, such as carbon nanotubes and nanofibers, have been studied as possible EC electrode materials. They have larger surface areas than conventional activated carbon and thus offer higher capacitance. Recent studies have suggested that carbon materials with nanopore structures can exhibit even higher capacitance, ostensibly because ions in confined geometries are stripped of their solvating molecules, which decreases their effective size.¹¹

The ECs described so far derive their capacitance from the electric double layer alone and are specifically referred to as electric double-layer capacitors (EDLCs). Another class of ECs, pseudocapacitors, employ faradaic processes but still behave like capacitors.¹² The fast and reversible faradaic processes at the electrode surfaces, in combination with the nonfaradaic formation of the electric double layer, allow pseudocapacitors to store much more energy than EDLCs. For instance, pseudocapacitor electrodes made of RuO_2 adsorb and desorb hydrogen, theoretically providing a gravimetric capacitance of 1358 F/g.

Although RuO_2 is an attractive material for high-performance pseudocapacitors, its cost has precluded any practical use. Alternatives include conducting polymers such as polythiophene, which can store energy through doping and dedoping of ions from the electrolyte.¹³ An advantage of conducting polymers is that one can, via appropriate choice of materials, tune the operational voltage of the

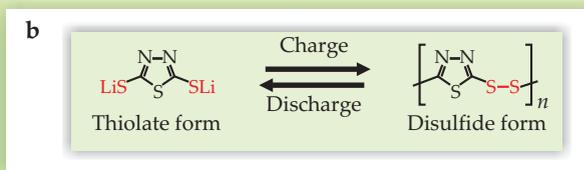
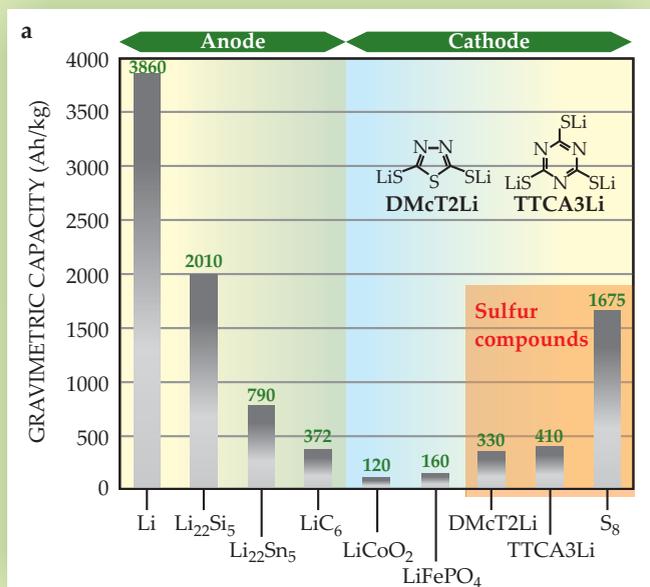


Figure 3. (a) Theoretical gravimetric capacities for lithium-ion battery electrode materials. Li metal is the highest-capacity anode material, but its use poses safety issues. Graphite, which intercalates Li ions to form LiC₆, is more often used in practice. Among cathode materials, organosulfur compounds such as DMcT2Li and TTCA3Li have significantly higher gravimetric capacities than the commonly used metal oxides and phosphates. Elemental sulfur is shown for comparison to the organosulfur compounds. **(b) Charge and discharge reactions** of the thiolate compound DMcT2Li, where n represents a large number of units that connect to form a polymer. The thiolate (S⁻) groups attract Li ions when the battery is discharged and bind to one another when the battery is recharged.

pseudocapacitor. However, polymer-based pseudocapacitors have poor charge–discharge cyclability compared to EDLCs because the redox processes degrade the molecular structure of the electrode materials.

Pseudocapacitors have energy densities of about 30 Wh/kg, more than EDLCs but still much less than LIBs, which today can average about 150 Wh/kg. Researchers have therefore focused on designing new materials to enhance a pseudocapacitor’s charge capacity while maintaining the device’s high power and exceptional charge–discharge cyclability. Organic materials capable of reversible multi-electron transfer have been recently studied and appear most promising.¹⁴

A third class of ECs are the asymmetric hybrid capacitors, which combine a nonfaradaic, or capacitor-type, electrode with one that is faradaic, or battery-type. The battery-type electrode provides high energy output, and the capacitor-type electrode provides high power. The high energy output is mainly due to the fact that the energy stored in a capacitor is proportional to the square of the cell voltage, as shown in figure 5. For instance, the combination of a carbon anode predoped with Li ions and an activated carbon cathode exhibits one of the highest energy outputs among ECs, because the Li redox chemistry allows an operating vol-

age of about 4 V, higher than any other EC.

Outlook

Major challenges for electrical energy storage devices include enhancing energy and power densities and charge–discharge cyclability while maintaining stable electrode–electrolyte interfaces. The need to mitigate the volumetric and structural changes in the active electrode sites that accompany ion intercalation and deintercalation—particularly in the case of metal oxides—has prompted researchers to look at nanoscale systems. Synthetic control of materials’ architectures at the nanoscale could lead to transformational breakthroughs in key energy storage parameters.¹⁵ For example, tailored nanostructured materials with very high surface areas could offer high and reproducible charge-storage capabilities and rapid charge–discharge rates. The development of revolutionary three-dimensional architectures is a particularly exciting possibility.¹⁶

The electrolyte is often the weak link in an energy storage device, due at least in part to the fact that many batteries and ECs operate at potentials beyond the thermodynamic stability limits of electrolyte systems. As a result, irreversible chemical reactions create films of solid material on the electrode surfaces, which affect the operation of the devices but

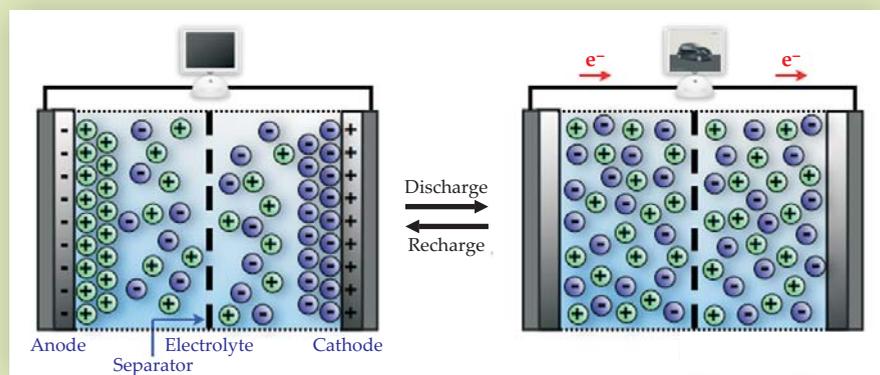


Figure 4. Charging and discharging an electric double-layer capacitor. When the capacitor is charged, ions from the electrolyte are attracted to the charged electrodes. The rigid separator acts to prevent a short circuit.

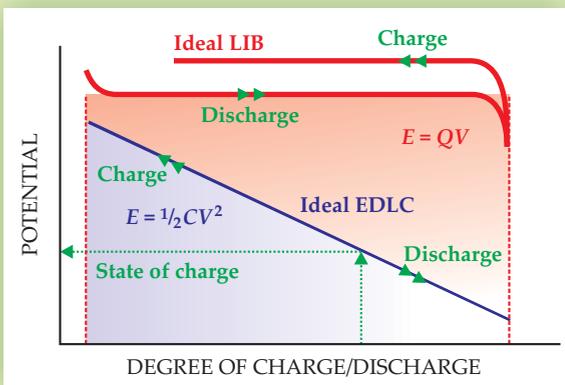


Figure 5. During discharge, the cell voltage on an ideal lithium-ion battery remains constant. But the voltage on an ideal electric double-layer capacitor decreases linearly. As a result, the energy E stored in the LIB is proportional to the voltage V , whereas the energy stored in the EDLC is proportional to the voltage squared. Moreover, the voltage provides a convenient measure of the amount of charge left, or state of charge, in EDLCs, but not in LIBs.

are difficult to control in a rational fashion. At present, interactions among the ions, solvent, and electrodes in electrolyte systems are poorly understood. Fundamental research will provide the knowledge base that will permit the formulation of novel electrolytes of deliberate design, such as ionic liquids and nanocomposite polymer electrolytes, which will enhance the performance and lifetimes of energy storage devices.

It is also important to understand the interdependence of the electrolyte and electrode materials, especially with regard to charge transfer and ion transport that take place at the interfaces. Electrode–electrolyte interfaces are complex and dynamic and need to be thoroughly characterized so that the paths of electrons and attendant ion traffic may be directed with exquisite fidelity. New analytical tools are needed to observe the dynamics at the interfaces, in situ and in real time. The information such tools will provide should allow for rational materials design, which will in turn lead to novel materials that have longer charge–discharge lifetimes and can store more energy.

Advances in computational methods will provide the understanding needed to make groundbreaking discoveries. Theory, modeling, and simulation can offer insight into mechanisms, predict trends, identify novel materials, and guide experiments. Large multiscale computations that integrate methods over broad spatiotemporal regimes have the potential to provide a fundamental understanding of processes such as phase transitions in electrode materials, charge transfer at interfaces, electronic transport in electrodes, and ion transport in electrolytes, and thereby pave the way for future electrical energy storage technologies.

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