

Batteries and a Sustainable Modern Society

by John B. Goodenough

After outlining the urgent need for realization of clean electrical energy generated by the sun for a sustainable modern society and the constraints of electrochemistry for this realization in a low-cost, safe rechargeable battery of long cycle life, recent advances in materials chemistry are outlined that provide an optimistic view that this realization may be possible in the relatively near future.

All life on Earth is sustained by the conversion of solar energy into chemical energy by plants. The chemical energy stored in plants is delivered to mobile life by metabolic processes and to society by man as the heat of combustion with its attendant emission of polluting gases. Modern society has become dependent on the solar energy stored over millennia in fossil fuels; this energy store has allowed the exploitation of the resources of the planet Earth in a throw-away economy, which is not sustainable without recycling of these resources. The combustion of fossil fuels is not recyclable, and the attendant massive emission of gases contributes to global warming and can choke the inhabitants of large cities. Although the energy from fossil fuels can be supplemented by nuclear energy that delivers heat without the gases of combustion, nuclear energy is neither clean of pollutants nor as convenient as the energy stored in liquid or gaseous fuels. In summary, a modern society is not sustainable unless means other than plants are developed to harvest and store the sun's energy and to deliver that energy as clean electric power without the pollutants from hydrocarbon combustion or the thermodynamic constraints on the efficiency of conversion of heat energy.

Harvesting of the sun's radiant energy by other means than by plants is possible with photovoltaic cells that convert it to electric power; nature converts it to hydropower and wind. The mechanical energy of hydropower can be stored in dams for conversion into electric power and windmills can convert wind energy into electric power. The heat delivered by nuclear fission is also transformed into electric power. The constant electric power delivered by nuclear energy needs to be stored for delivery to a variable demand or only used for the constant component of demand. On the other hand, radiant-solar and wind energies are diffuse and variable on diurnal and seasonal time scales. Although the electric power delivered by photovoltaic cells and windmills may be locally collected and transported over long distances, it needs to be stored for delivery as clean electric energy to a variable demand that may be either portable or stationary, distributed or centralized. A convenient long-term energy store of electrical energy as chemical energy that is delivered back as electrical energy is the rechargeable battery; the efficiency of the energy conversions in a battery is not constrained by thermodynamics other than by the heat loss associated with the internal battery resistance. Although the energy stored in the electrodes of a rechargeable battery is less dense and less versatile than the energy stored in a fossil fuel, its delivered energy is clean and can be portable. The challenge to the material chemist/engineer is to develop, with environmentally friendly materials, rechargeable batteries of high energy density that are safe and efficient with a long cycle and shelf life at a cost low enough to be commercially viable.

There are three principal markets for a rechargeable battery: (1) powering portable hand-held devices, (2) powering electric road vehicles, and (3) stationary distributed or centralized electrical energy storage to supplement energy storage in the grid. Powering of hand-held devices does not compete with fossil fuels, which is why today's Li-ion batteries are ubiquitous. Powering electric vehicles for road transportation must compete with the internal combustion engine powered by a liquid fuel, normally a fossil fuel, of high energy density.

The hidden cost to the environment and to the economy for securing access to the fossil-fuel sources are not apparent to the individual customer at the gasoline pump. Increasing safely the volumetric energy density of a battery cell beyond that of a Li-ion battery at temperatures to -20°C is critical for batteries that power an electric vehicle. These batteries store and deliver dc electric power, so they are charged more efficiently by electric power from solar energy than from wind energy. The ac power from wind energy is more efficiently stored directly into the grid than in a rechargeable battery. For stationary electrical energy storage, the amount and cost, including shelf and cycle life, of energy stored in a single charge is more critical than the volumetric energy density and operation at low temperatures.

Battery Constraints

Battery Stack

A battery may consist of an assembly of identical cells assembled in parallel to give a desired output current I_b and in series to give a desired voltage V_b to deliver a power $P_b = I_b V_b$ over a time Δt_b . The larger the amount of power that can be delivered by the individual cell, the fewer the number of cells that are needed in a battery for a given application and, therefore, the simpler the management of a stack of cells. The larger the area of the cell electrodes, the fewer the number of cells that need to be connected in parallel. Therefore, the material chemist/engineer concentrates initially on the performance per unit area of an individual cell, which normally begins with the design and testing of a cell the size of a large coin, i.e., a "coin cell"; but scaling to a large-area cell must be considered in the design of low-cost cell components.

Components of a Battery Cell

Figure 1 illustrates schematically a typical battery cell and the energies of the electronic states in the two electrodes and the electrolyte that separates them. A battery cell stores electrical energy as chemical energy in its two electrodes; the *anode* is the reductant and the *cathode* is the oxidant of the chemical reaction in a cell. The energy difference between the chemical potentials μ_A of the anode and the μ_C of the cathode is

$$\mu_A - \mu_C = eV_{oc} \quad (1)$$

where V_{oc} is the open-circuit voltage of the cell and e is the magnitude of the electron charge. The two electrodes are electronic conductors during charge and discharge so the μ_A and μ_C become the Fermi levels of the two electrodes. The two electrodes are separated by an *electrolyte* that conducts the ionic component of the chemical reaction between the electrodes but is an electronic insulator to force the electronic component into an external circuit that carries the current I . The mobile ion inside the cell is the *working ion*; it is normally a monovalent cation, but it may be an oxide ion or a multivalent cation. If the electrolyte is a liquid, the electrodes are kept apart by a porous *separator* that does not react with either electrode and is permeated by the liquid electrolyte. The *energy window* of the electrolyte is

$$E_g = \text{LUMO} - \text{HOMO} \quad (2)$$

where the LUMO and HOMO are, respectively, the energies of the lowest-unoccupied and highest occupied molecular orbitals. An anode with a $\mu_A > \text{LUMO}$ reduces the electrolyte unless (or until) the reaction

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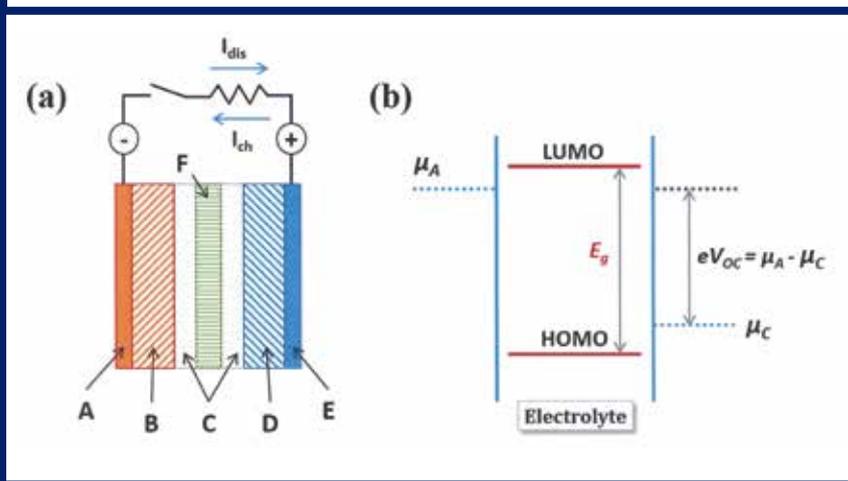


Fig. 1. (a) Schematic of a battery cell. A = anode current collector, B = anode (reductant), C = electrolyte, D = cathode (oxidant), E = cathode current collector, F = separator. (b) Anode μ_A and cathode μ_C electrochemical energies relative to energy gap E_g of the electrolyte for a stable shelf life.

is pacified by the formation of a solid-electrolyte interphase (SEI) that is an electrolyte layer with a LUMO $> \mu_A$. Similarly, a $\mu_C < \text{HOMO}$ oxidizes the electrolyte unless (or until) the cathode reaction is pacified by an SEI surface layer with a HOMO $< \mu_C$.

A solid electrolyte may act as a separator or as an interfacial layer in contact with an electrode on one side and a liquid electrolyte on the other side. In the latter case, the solid (crystalline, glass, amorphous mass, or polymer) may be referred to as the SEI across which the electrochemical potential of a solid electrode is lowered or raised to prevent a liquid electrolyte from being reduced by an anode with $\mu_A > \text{LUMO}$ or being oxidized by a cathode with $\mu_C < \text{HOMO}$ in Fig. 1b. Since the ionic conductivity inside the cell is much smaller than the electronic conductivity in the external circuit, a thin electrolyte is sandwiched between two large-area electrodes each contributing electronic conduction to a metallic current collector that delivers the electrons of the chemical reaction between the electrodes to the external circuit. The electrodes of a cell must make electronic contact with the current collector as well as ionic contact with the electrolyte, so small-particle reactants must be attached to or make contact with an electronically conducting porous matrix that contacts the current collector and is permeated by the electrolyte. This constraint limits the volumetric energy density of a small-particle electrode and, therefore, its application to a battery that powers a road vehicle.

It should be noted that at open-circuit, only the electronic component of the chemical reaction between the electrodes is stopped; the ionic component inside the cell continues until the internal electric field between the electrodes make $\mu_A = \mu_C$. Whether the working ion is a cation or an anion, the cathode becomes positively charged and the anode negatively charged. That is why the cathode is the positive electrode of a battery at open circuit having a V_{oc} of Eq. (1).

Electrical Energy Storage

Density of Stored Energy ▶ The density of stored energy in a cell delivering electric power $P = IV(q)$ at a constant current $I = dq/dt$ is

$$\Delta E = \int_0^{\Delta t} IV(q)dt = \int_0^{Q(I)} V(q)dq = \langle V(q) \rangle \cdot Q(I) \quad (3)$$

where q is the state of charge and $Q(I)$ is the capacity, which is the amount of electronic charge per weight or volume that is delivered over the time Δt to complete the chemical reaction between the two electrodes:

$$Q(I) = \int_0^{\Delta t} Idt = \int_0^{Q(I)} dq \quad (4)$$

Efficiency of Electrical Energy Storage ▶ In a rechargeable battery, the chemical reaction of each cell is reversible; chemical energy can be restored by reversing the discharge current I_{dis} by applying a charging power $P_{ch} = I_{ch}V_{ch}$. The efficiency of energy storage is $100 P_{dis}/P_{ch}$ % with

$$V_{ch} = V_{oc} + \eta_{ch} \quad \text{and} \quad V_{dis} = V_{oc} - \eta_{dis} \quad (5)$$

The η_{ch} and η_{dis} are called the overvoltage (or the polarization) on charging and discharging, respectively, resulting from the internal battery resistance $R_b = R_{el} + R_{ct}$, where R_{el} is the resistance to the transport of the working ion in the electrolyte and R_{ct} is the sum of the resistance to ionic transport across electrode/electrolyte interfaces and any solid/liquid interfaces within a complex electrolyte.

The Coulombic efficiency in a rechargeable cell is the recovery of stored charge in a charge/discharge cycle ($100 Q_{dis}(I)_{n+1}/Q_{ch}(I)_n$ %). The capacity fade is a measure of the drop in cell capacity ($100 Q(I)_{n+1}/Q(I)_n$ %) between charge/discharge cycle numbers $(n+1)$ and n . Cycle life is the number of cycles before $Q(I)$ drops to 80% of its

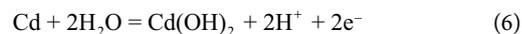
starting value, which may be taken a few cycles after the initial charge where there is a large irreversible capacity loss in the first few cycles as a result of physical and/or chemical adjustments of the electrode. Capacity fading is the result of irreversible changes that occur in $Q(I)$ as a result of the volume changes of the electrodes on cycling, but in the initial few charges of a cell assembled in a discharged state, capacity loss may also be the result of formation of an SEI at the anode in which the working ion is provided by the cathode.

From Fig. 1b and Eq. (1), the V_{oc} of a cell may be limited either by the inability to synthesize a cathode with μ_C more than 5 eV below the μ_A of metallic lithium, which normally makes $V_{oc} \leq 5$ V, or by the energy window of the electrolyte, Eq. (2). The SEI's obtained with soluble additives in an organic-liquid electrolyte are amorphous electrolytes; these SEI's may continue to form during a charge if the volume changes in an active electrode particle increase the electrode/electrolyte interface area by dendrite growth or by cracking the particle to create new surface area, thus contributing to capacity fade. If a solid (ceramic, glass, or polymer) electrolyte is stable on contact with an electrode surface, it can act as the SEI if the interface area is kept constant by a wetting of the electrolyte surface by the electrode.

Electrolyte Problem

Aqueous Electrolytes

A conventional rechargeable cell uses an aqueous electrolyte, either alkaline or acidic, in which H^+ is the working ion. With an alkaline electrolyte, the charged cathode is a layered NiOOH into which H^+ is inserted reversibly on discharge to create Ni(OH)₂. The Ni(III)/Ni(II) redox energy of this oxyhydroxide is well-matched to the HOMO of a liquid KOH electrolyte. The Fermi energy of Cd in a Ni-Cd cell is well-matched to the electrolyte LUMO in the reversible reaction.



where the Cd(OH)₂ mass remains near the anode surface. Alternatively, a metal-hydride MH_x is an insertion host that releases $\text{H}^+ + \text{e}^-$ on discharge and reforms on charge. A zinc/air battery uses gaseous oxygen as the cathode reactant, which requires development of inexpensive catalysts attached to a metallic substrate for the oxygen-reduction reaction (ORR) $\text{O}_2 + 4\text{e}^- + 4\text{H}^+ = 2\text{H}_2\text{O}$ on discharge and, on charge, for the reverse oxygen evolution reaction (OER) of O from $2\text{H}_2\text{O}$. However, the 1.23 eV energy window of an aqueous electrolyte limits a long shelf life to a $V_{oc} \leq 1.5$ V. For example, the 2-V lead-acid battery does not have a long shelf life in partially discharged states owing to the agglomeration and crystallization of the insulating product PbSO_4 , which is called sulfation.

Organic-Liquid Electrolyte

An organic-liquid electrolyte has a window $E_g \approx 3.0$ eV, but the H^+ ion is not mobile in these electrolytes. However, the Li^+ , Na^+ , and K^+ ions can be released from soluble-salts to give a working-ion conductivity $\sigma_i = 10^{-2}$ to 10^{-1} S cm^{-1} at 25°C. Since an alkali metal is immiscible with an organic-liquid electrolyte, dendrites commonly form and grow during plating across an alkali-metal/organic-liquid interface; the dendrites can grow across a thin electrolyte to the cathode to give an internal short-circuit with incendiary consequences if the electrolyte is flammable. As a result, batteries containing an organic-liquid electrolyte do not use a solid alkali-metal anode. The first Li-ion battery used layered graphite into which Li is intercalated reversibly to LiC_6 with a loss of only about 0.2 V in V_{oc} , but on a fast charge, V_{ch} becomes large enough to plate lithium on the carbon anode. Therefore, the rate of recharge of the Li-ion battery with a carbon anode has been slow. Another difficulty with the carbon anode is a $\mu_A > LUMO$ of the organic-liquid electrolyte, which has required introduction of an additive into the electrolyte to form an SEI during charge, and the Li^+ of the SEI is robbed from the cathode on the first charge since the battery is assembled in a discharged state to keep the anode free of metallic lithium. It is the volumetric capacity of the cathode that limits the volumetric energy density $\langle V(q) \rangle \cdot Q(l)$ of a cell. Nevertheless, the layered $Li_{1-x}Co_{1-y}Ni_yO_2$ cathode gives a voltage $V_{oc} \approx 4.0$ V versus Li^+/Li^0 for $0 \leq y \leq 0.5$, which is well-matched to the HOMO of an organic-carbonate liquid electrolyte and it is metallic, which allows the use of large particles needed for a large volumetric energy density.

Two approaches have been used to increase the rate of charge of a Li-ion battery: the use of (1) an insertion-compound anode having a V_{oc} more than 1.2 V lower than with a metallic-lithium anode, e.g., the spinel $Li[Li_{1/3}Ti_{5/3}]O_4$ and layered $Li_xTiNb_2O_7$; (2) a Si, Sn, or Sb anode forming an alloy of large capacity with Li at a V_{oc} over 0.4 V below that with a metallic-lithium anode. A large volume expansion on alloying, over 300% in the case of Si, has been thought to make it necessary to fabricate the anode as an assembly of small particles embedded or encapsulated in carbon or a polymer, which lowers the volumetric capacity and leaves a large anode surface area for SEI formation. Nevertheless, the Eneate Co. has developed a novel geometry for a Si anode that gives a large capacity and cycle life with a fast charge. Conversion reactions in which Li insertion displaces a cation have also been investigated, but these also involve a volume change. The realization of a safe alkali-metal anode promises to provide the needed energy density and cycle life.

Polymer-gel/Oxide Composites

A polymer gel is a porous polymer membrane permeated by a liquid electrolyte. The polymer and oxide of the separator needs to be chemically stable on contact with both the anode and the cathode. Low-cost polymer gels have been fabricated as cross-linked membranes with thiolene chemistry. The addition of inexpensive oxide particles, e.g., Al_2O_3 , SiO_2 , or Sb_2O_3 , can be used to block anode dendrites from crossing over to the cathode; the oxides strengthen, but reduce the flexibility, of the polymer membrane. Alternatively, a glass-fiber membrane has been used as the oxide component with a polymer coat leaving the glass-fiber membrane sufficiently porous for permeation by a liquid electrolyte. These membranes are better Li^+ or Na^+ conductors if the mobile ions are exposed only to F^- or $C=O$ terminal species on the polymer; the terminal $C-O^-$ of polyethylene oxide attracts Li^+ too strongly for fast Li^+ transport. Metal-organic framework (MOF) compounds can also be fabricated as membranes that can absorb a liquid electrolyte. These several different membrane separators may be used as separators in flow-through batteries having organic-liquid electrodes containing a soluble redox molecule; an organic liquid electrolyte allows choosing redox molecules that give a higher voltage and a more stable separator than the Nafion membrane used in today's aqueous-electrolyte flow-through battery.

Although these polymer-gel/oxide composite separators can block dendrites from an alkali-metal anode, they do not solve the anode problem; dendrite formation and growth continues to create new anode surface area on charge and, therefore, more SEI area to generate an irreversible loss of Li^+ from the cathode to give a continuing capacity fade.

Solid Electrolytes

The safety hazard with a flammable organic-liquid electrolyte has stimulated work on solid electrolytes for an all-solid-state battery. A solid electrolyte may be a ceramic, a glass, or a polymer. A dry polymer electrolyte is preferred since crystalline electrodes change volume on charge/discharge cycling and maintenance of a stable ionic contact across an interface between a crystalline electrode and a ceramic or glass electrolyte in a rechargeable battery is a challenge, particularly for the cathode. However, on the anode side, plating/stripping of a metallic anode can restrain the anode volume change to be perpendicular to the interface if the anode wets the surface of both the electrolyte and the current collector. A challenge is to develop a Li^+ or Na^+ dry-polymer electrolyte with an ionic conductivity $\sigma_i > 10^{-3}$ S cm^{-1} at room temperature and a LUMO above the Fermi energy of the alkali-metal anode. A promising strategy for meeting this challenge is to develop a cross-linked polymer membrane containing pendant molecules extending into the interstitial space that neither attract the mobile alkali ion strongly nor impede its motion. However, if the mobile ion is introduced with a salt, the movement of the salt anion away from the anode surface may create a local electric-double-layer capacitance that lowers the voltage for the onset of an anode-polymer chemical reaction. This problem can be addressed.

Meanwhile, a glass-solid electrolyte having a $\sigma_i > 10^{-2}$ S cm^{-1} and an activation energy for ionic motion that is < 0.1 eV has been developed and shown to be wet by an alkali-metal anode. The long-term stability of the solid/solid interface is under testing. These developments promise to provide a step improvement in the energy density, rate of charge, and cycle life of a rechargeable alkali-metal battery cell.

The cathode of an all-solid-state battery cell commonly consists of particles bonded to an electronically conducting fiber or porous mass that allows particle access on discharge to both the electrolyte working ions and electrons from the cathode current collector. If the chemically active cathode particles are electronic insulators, they need to be small particles, which makes difficult realization of a large volumetric capacity. To date, all-solid-state batteries with a ceramic solid electrolyte have had a small capacity. However, a small amount of liquid or polymer electrolyte contacting the cathode would not pose a safety problem and would allow use of conventional strategies for a high-capacity cathode.

Electric power can also be stored in an electric-double-layer capacitance at an electrode/electrolyte interface. This strategy is used in an *electrochemical capacitor*, commonly called a *supercapacitor*. A Li^+ or Na^+ glass electrolyte having a huge dielectric constant because of the presence of electric dipoles has recently been reported. With this electrolyte and high-surface-area metallic electrodes, supercapacitors with an electric-power-storage capacity approaching (overlapping) that of present-day rechargeable batteries, but with a much more rapid charge/discharge and longer cycle life, may be achieved. The exploration of cycling cells with current collectors of widely different Fermi levels is in its infancy, and the electrochemical performance of cells that combine a chemical as well as a capacitive storage of electric power remains relatively unexplored.

The Cathode Problem

Insertion Compound Hosts

The capacity of the cathode limits the capacity of a cell and, therefore, the volumetric energy density of a rechargeable battery cell, Eq. (3). Today's Li-ion batteries commonly use layered $Li_{1-x}Co_{1-y}Ni_yO_2$ particles embedded in carbon permeated by an organic-liquid electrolyte. The capacity of the cathode is limited by the solid-solution range of Li in the layers between the close-packed $Co_{1-y}Ni_yO_2$ layers; oxygen is evolved for $x > x_c = 0.55$ with $y = 0$, but the oxygen evolution may be delayed to a larger x_c for $y \leq 0.8$. However, a $y = 1$ doesn't result in good ordering of the Li into alternate layers of the structure. The loss of oxygen from the cathode on a deep charge requires monitoring the cell charge as well as the rate

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of charge to restrict the Li extraction to $x < x_c$. On the other hand, a $\text{Li}_{1-x}[\text{Ni}_{1-2y}\text{Mn}_y\text{Co}_y]\text{O}_2$ layered oxide permits extraction to $x_c = 1$ provided $y < 1/3$ is small enough to keep the voltage to $V < 4.75$ V.

The development of a metallic insertion compound for a sodium-ion rechargeable battery has proven more difficult. The cyanoperovskite structure of Prussian blue, e.g., $\text{Na}_2\text{MnFe}(\text{CN})_6$, offers an insertion-host cathode particle with an acceptable specific capacity on a fast (5C) charge/discharge cycle down to temperatures $T < -20^\circ\text{C}$; but the poor electronic conductivity requires attachment of relatively small cathode particles onto electronically conducting fibers that contact the cathode current collector and also allow absorption of an organic-liquid electrolyte to provide the active particles access to the working ions of the electrolyte. The small size of the active particles has prevented realization of the needed volumetric energy density for a battery powering an electric road vehicle. Whether the recent discovery of growth of Prussian-blue particles at defects in carbon nanotube fibers can provide the needed volumetric energy density is yet to be determined.

Alternative Cathodes

The highest specific-energy cathodes would use an element capable of reacting with two alkali-metal cations per cathode atom as is illustrated by the reactions $16\text{Li} + \text{S}_8 = 8\text{Li}_2\text{S}$ and $4\text{Li} + \text{O}_2 = 2\text{Li}_2\text{O}$. These reactions have prompted a strong effort to develop an S_8 and an air (O_2) cathode with a metallic-lithium anode. The use of a gaseous air cathode has, to date, been restricted to cells with an aqueous electrolyte. Higher voltages could be obtained with a solid electrolyte stable in water, but those stable in water have not been stable on contact with an alkali-metal anode. Use of a Li^+ or Na^+ polymer electrolyte on the anode side of a solid electrolyte stable in water may allow realization of a Li-air or Na-air rechargeable battery; low-cost transition-metal oxide catalysts for a Li-air battery are known.

Much work has been devoted to the development of a viable sulfur cathode in an organic-liquid electrolyte. The intermediate species Li_2S_x with $2 \leq x \leq 8$ are soluble in the organic-liquid electrolyte, and the soluble molecules may move to the anode or to an insulator separator surface where they are not oxidized back to a solid molecule on charge, thereby producing a rapid capacity fade. The development of a cathode architecture that confines the charged S_8 particles in mesoporous conductive fibers and/or captures soluble species on conductive surfaces making contact with the cathode current collector

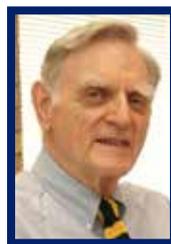
has prohibited realization of a sulfur cathode with sufficient volumetric capacity for an electric vehicle. An all-solid-state cell with the glass electrolyte, a metallic-lithium anode, and a sulfur relay embedded in a carbon/glass mix on a copper current collector plates reversibly the anode lithium on the cathode during discharge which introduces a new battery-cell concept of exceptional performance.

The discovery of a glass electrolyte having a huge dielectric constant and a stability to 10 V versus Li^+/Li^0 may offer electric double-layer capacitors of larger capacity for storage of electrical energy. These capacitors provide an extremely fast discharge and exhibit no capacity fade on cycling. All that is required, in addition to the glass electrolyte, is a metallic cathode having a large surface area contacting the electrolyte.

In summary, the advent of fast alkali-ion polymer and glass electrolytes that permit reversible plating/stripping of metallic-lithium or metallic-sodium anodes appears to permit realization in the near future of safe, rechargeable lithium and sodium batteries with sufficiently low cost and cycle life for commercially viable, clean electrical energy storage that can be competitive with the energy stored in a fossil fuel. ■

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About the Author



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From 1976-1986, he was Professor and Head of the Inorganic Chemistry Laboratory of the University of Oxford, England, where he developed the cathodes that have enabled the Li-ion battery, and since 1986 he has held the Virginia H. Cockrell Centennial Chair of Engineering at The University of Texas at Austin where he has continued the development of the rechargeable battery, catalytic electrodes for the solid oxide fuel cell, and the use of high pressure to study the transition from localized to itinerant d electrons in transition-metal oxides. He may be reached at jgoodenough@mail.utexas.edu.