REVIEW

Electrical Energy Storage for the Grid: A Battery of Choices

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The increasing interest in energy storage for the grid can be attributed to multiple factors, including the capital costs of managing peak demands, the investments needed for grid reliability, and the integration of renewable energy sources. Although existing energy storage is dominated by pumped hydroelectric, there is the recognition that battery systems can offer a number of high-value opportunities, provided that lower costs can be obtained. The battery systems reviewed here include sodium-sulfur batteries that are commercially available for grid applications, redox-flow batteries that offer low cost, and lithium-ion batteries whose development for commercial electronics and electric vehicles is being applied to grid storage.

The August 2003 blackout in the Northeast and the recent September 2011 power failure that extended from Southern California to Mexico and Arizona are two of the more widely publicized examples in which power outages affected many millions of consumers. From a broader perspective, such power outage events underscore the complex set of issues associated with the generation and use of electricity: the reliability of the grid, the use of fossil fuels and related carbon emissions, the development of electric vehicles to decrease dependence on foreign oil, and the increased deployment of renewable energy resources. Underlying these considerations is the recognition that inexpensive and reliable energy is vital for economic development. Moreover, most of these issues are international in scope, with the additional caveat that worldwide demand for electricity is projected to double by 2050.

Electrical energy storage (EES) cannot possibly address all of these matters. However, energy storage does offer a well-established approach for improving grid reliability and utilization. Whereas transmission and distribution systems are responsible for moving electricity over distances to end users, the EES systems involve a time dimension, providing electricity when it is needed. A recent study identified a number of high-value applications for energy storage, ranging from the integration of renewable energy sources to power quality and reliability (*1*). Despite the anticipated benefits and needs, there are relatively few storage installations in operation in the United States. Only ~2.5% of the total electric power delivered in the United States uses energy storage, most of which is limited to pumped hydroelectric storage. This is far below the energy storage levels in Europe (10%) and Japan (15%), where more favorable economics and policies are in place (*2*).

Energy storage technologies available for large-scale applications can be divided into four types: mechanical, electrical, chemical, and electrochemical (*3*). Pumped hydroelectric systems account for 99% of a worldwide storage capacity of 127,000 MW of discharge power. Compressed air storage is a distant second at 440 MW. The characteristics for several of these EES systems in terms of power rating, which identifies potential applications, and duration of discharge are illustrated in Fig. 1. Potential grid applications range from frequency regulation and load following, for which short response times are needed, to peak shaving and load shifting, both of which can lead to improvements in grid reliability, stability, and cost (*4*). The electric power profile shown in fig. S1 indicates how storage can integrate renewable resources and be used to accommodate peak loads. Load shifting represents one of the more tantalizing opportunities for EES because of the benefit in storing energy when excess power is generated and releasing it at times of greater demand. The technical requirements, however, are quite rigorous.

As indicated in Fig. 1, there are several energy storage technologies that are based on batteries. In general, electrochemical energy storage possesses a number of desirable features, including pollution-free operation, high round-trip efficiency, flexible power and energy characteristics to meet different grid functions, long cycle life, and low maintenance. Batteries represent an excellent energy storage technology for the integration of renewable resources. Their compact size makes them well suited for use at distributed locations, and they can provide frequency control to reduce variations in local solar output and to mitigate output fluctuations at wind farms. Although high cost limits market penetration, the modularity and scalability of different battery systems provide the promise of a drop in costs in the coming years. Today, sodium/sulfur (Na/S) battery technology is commercially available for grid applications, with some 200 installations worldwide, accounting for 315 MW of discharge power capacity. Moreover, there are emerging opportunities for other battery systems because of potential low cost (redox-flow) and enhanced performance [lithium (Li)–ion]. In this Review,

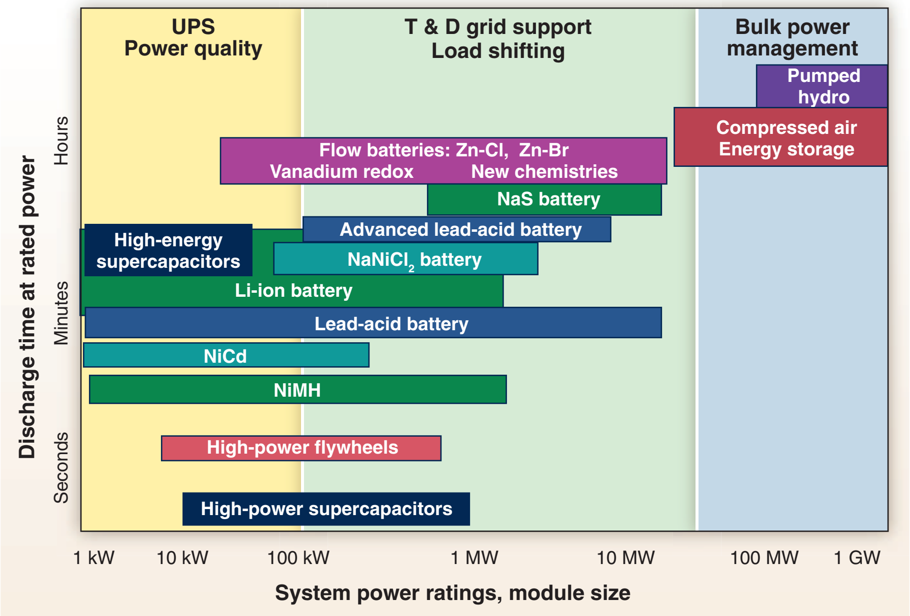

Fig. 1. Comparison of discharge time and power rating for various EES technologies. The comparisons are of a general nature because several of the technologies have broader power ratings and longer discharge times than illustrated (*1*). [Courtesy of EPRI]

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we present some of the overarching issues facing the integration of energy storage into the grid and assess some of the key battery technologies for energy storage, identify their challenges, and provide perspectives on future directions.

Utility Perspective on Energy Storage

EES has often been described as the "Holy Grail" of the electric utility industry. This phrase evokes the eagerness of utilities and other stakeholders to achieve cost-effective storage options, which could potentially cure many of the ills faced by the electric power enterprise. However, the phrase Holy Grail also suggests that the search for energy storage will be long, difficult, and perilous. We are unlikely to find, at least in the near term, a single technology that can repeatedly and efficiently store large quantities of electric energy at low cost. On the other hand, a portfolio approach that is based on using a combination of technologies may be the most effective means to introduce and integrate energy storage.

The usefulness of EES stems from the operational characteristics of the grid as a supply chain of a commodity, electric power. At present, the electric power infrastructure functions largely as a just-in-time inventory system in which a majority of energy is generated and then transmitted to the user as it is consumed. Without the ability to store energy, there must be sufficient generation capacity on the grid to handle peak demand requirements, despite the likelihood that much of that capacity sits idle daily as well as for large portions of the year (fig. S2). Correspondingly, the transmission and distribution system must also be sized to handle peak power transfer requirements, even if only a fraction of that power transfer capacity is used during most of the year. Operationally, electrical power generation must be continuously ramped up and down to ensure that the delicate balance between supply and demand is maintained. The up and down cycling reduces power plant efficiency, resulting in higher fuel consumption and higher emissions per kilowatt-hour (kWh) produced. This procedure also causes more wear on the equipment and reduces the lifetime of power plants (*5*).

By decoupling generation and load, grid energy storage would simplify the balancing act between electricity supply and demand, and on overall grid power flow. EES systems have potential applications throughout the grid, from bulk energy storage to distributed energy functions (*1*). The availability of energy storage would help to eliminate the distinction between peak and baseload generation (fig. S1), allowing loads at any time to be serviced by the lowest cost energy resources (*6*).

Storage solutions based on the technologies we have today are so expensive that historically it has been far more cost-effective to expand generation as well as transmission and distribution to serve the peak load and provide sufficient operating margin to meet consumer demands for reliability. In those cases in which storage is used, pumped hydroelectric plants are generally involved. These plants are composed of low-cost materials (dirt, concrete, and water) that have a lifetime of over 40 years, minimal maintenance costs, and relatively high round-trip efficiency (between 65 and 75%). Although there are obvious limitations because of geographical considerations, pumped hydro will be the benchmark for grid-scale storage for years to come.

In the near term, utilities are aware of the rising need for EES solutions but are skeptical of the technologies that have been proposed to date. Even in cases in which technology has substantial merit, the absence of cost-effective products with a track record of safe and reliable operation has made the industry skittish about their use. Table 1 lists some of the current maturity levels for various energy storage technologies, their operational characteristics, and cost estimates. If successful, the outcomes from these projects may alleviate industry concerns of matters such as performance, cycle life, economics, and risks. Another promising development is that the industry has begun working to establish standards and targets.

Electrochemical Energy Storage

Electrochemical energy storage approaches can be distinguished by the mechanisms used to store energy (*7*). Batteries, regardless of their chemistry—aqueous, nonaqueous, Li or Na-based—store energy within the electrode structure through charge transfer reactions. By comparison, fuel cells, which are not rechargeable, store energy in the reactants that are externally fed to the cells. Both of these differ from redox-flow cells, which store energy in the redox species that are continuously circulating through the cells. Supercapacitors offer yet a different energy storage mechanism, via a capacitive process arising from an electrochemical double layer at the electrode-electrolyte interface. Each mechanism has different strategies that can be used to improve the power and energy densities of the EES approach.

Table 1. Energy storage for utility transmission and distribution grid support. The megawatt- and kilowatt-scale energy storage systems listed here have potential impact in several areas, including transmission and distribution substation grid support, peak shaving, capital deferral, reliability, and frequency regulation (*1*). [Courtesy of EPRI]

Technology option	Maturity	Capacity (MWh)	Power (MW)	Duration (hours)	% Efficiency (total cycles)	Total cost ($/kW)	Cost ($/kWh)
CAES (aboveground)	Demo	250	50	5	(>10,000)	1950–2150	390–430
Advanced Pb-acid	Demo	3.2–48	1–12	3.2–4	75–90 (4500)	2000–4600	625–1150
Na/S	Commercial	7.2	1	7.2	75 (4500)	3200–4000	445–555
Zn/Br flow	Demo	5–50	1–10	5	60–65 (>10,000)	1670–2015	340–1350
V redox	Demo	4–40	1–10	4	65–70 (>10,000)	3000–3310	750–830
Fe/Cr flow	R&D	4	1	4	75 (>10000)	1200–1600	300–400
Zn/air	R&D	5.4	1	5.4	75 (4500)	1750–1900	325–350
Li-ion	Demo	4–24	1–10	2–4	90–94 (4500)	1800–4100	900–1700

Although not discussed here, capacitive energy storage offers some promising opportunities for grid-scale applications (Fig. 1). Supercapacitors provide higher power and longer cycle life than that of batteries and are receiving renewed attention as researchers try to better understand fundamental interfacial processes and improve energy density (*8*). The technology is of interest for power quality applications, such as alleviating short-term disruptions of a few minutes until a generator, fuel cell, or battery can be placed in service. Because the lifetime costs for supercapacitors can be attractive (*6*), there is the prospect that this technology will be used in conjunction with batteries so as to provide future grid storage solutions.

A battery is composed of several electrochemical cells that are connected in series and/or in parallel in order to provide the required voltage and capacity, respectively. Each cell is composed of a positive and a negative electrode, which are where the redox reactions take place. The electrodes are separated by an electrolyte, usually a solution containing dissociated salts so as to enable ion transfer between the two electrodes. Once these electrodes are connected externally, the chemical reactions proceed in tandem at both electrodes, liberating electrons and providing the current to be tapped by the user (*9*, *10*). The energy storage properties for most of the common rechargeable batteries are shown in Fig. 2, with additional details provided in table S1.

Lithium Ion Batteries

The Li-ion battery (LIB) technology commercially introduced by Sony in the early 1990s is based on the use of Li-intercalation compounds. Li ions migrate across the electrolyte located between the two host structures, which serve as the positive and negative electrodes (Fig. 3). Li-ion batteries outperform, by at least a factor of 2.5, competing technologies [nickel (Ni)–metal hydride, Ni-cadmium (Cd), and lead (Pb)–acid)] in terms of delivered energy while providing high specific power (Fig. 2). The overwhelming appeal of Li-electrochemistry lies in its low molecular weight; small ionic radius, which is beneficial for diffusion; and low redox potential [$E°(\mathrm{Li}^+/\mathrm{Li}) = -3.04$ V vs standard hydrogen electrode (SHE)] (*11*). The latter enables high-output voltages and therefore high-energy densities. Such attractive properties, coupled with its long cycle life and rate capability, have enabled Li-ion technology to capture the portable electronics market and make in-roads in the power tools equipment field. LIBs are also regarded as the battery of choice for powering the next generation of hybrid electric vehicles (HEVs) as well as plug-in hybrids (PHEVs), provided that improvements can be achieved in terms of performance, cost, and safety (*12*). Because long-term stability, high-energy density, safety, and low cost are common to developing batteries for both automotive and grid applications, considerable synergy should exist between the two areas, although there will be certain differences. Figures of merit for electric vehicle applications call for a reduction in the price per kilowatt-hour by a factor of 2 and a doubling of the present energy density. The realization of such goals will be beneficial for grid storage systems, although with probably more emphasis on cost and less on energy density. Other differences between the two technologies include safety, which is easier to achieve in stationary situations than in mobile ones, whereas long cycle life is a key factor for grid applications. LIBs for vehicles require versatility in their energy and power capabilities in order to meet the needs of the various types of electric vehicles and the associated performance requirements, whereas LIBs for the grid are likely to be modular.

A number of advances have been made in the LIB field by controlling particle size in addition to composition, structure, and morphology in order to design better electrodes and electrolyte components (*13*). Decreasing electrochemically active materials to sub-micrometer and smaller

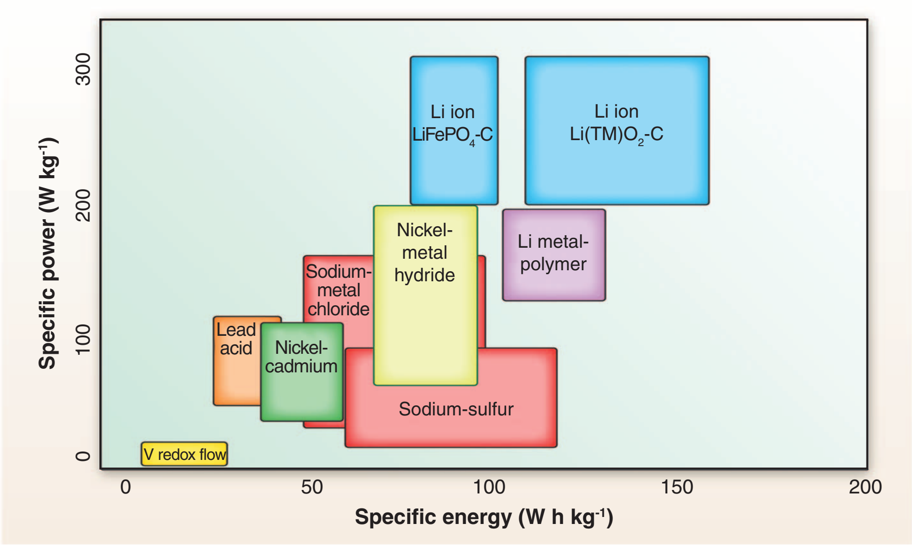

Fig. 2. Gravimetric power and energy densities for different rechargeable batteries. Most of these systems are currently being investigated for grid storage applications.

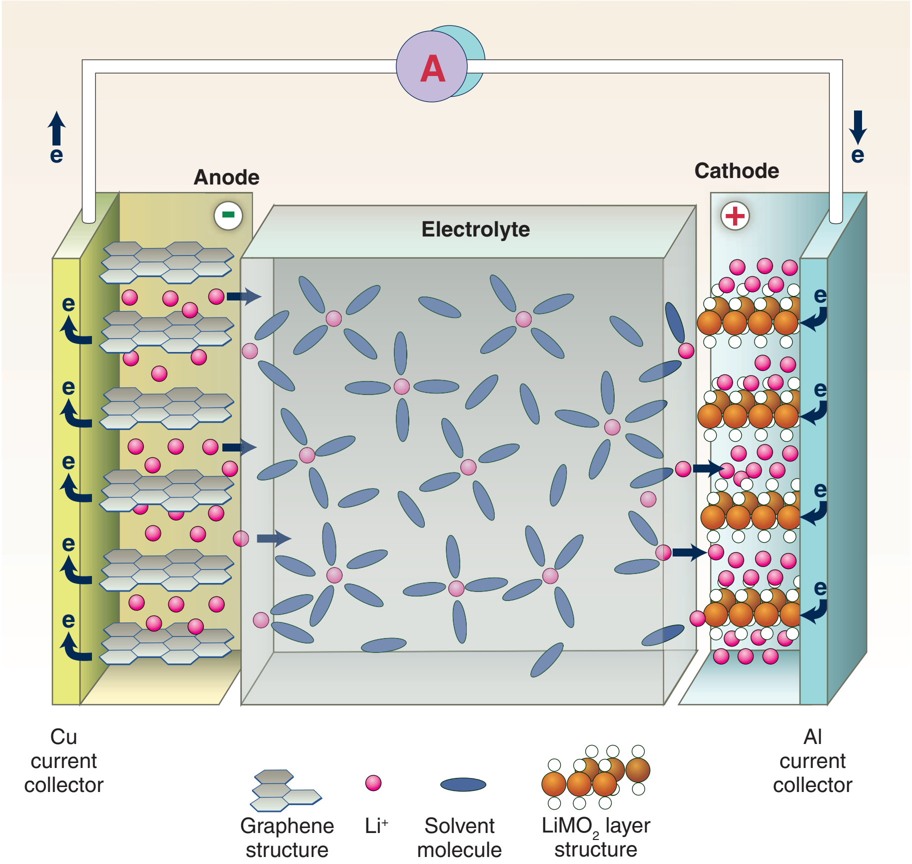

Fig. 3. Schematic of a LIB. The negative electrode is a graphitic carbon that holds Li in its layers, whereas the positive electrode is a Li-intercalation compound—usually an oxide because of its higher potential—that often is characterized by a layered structure. Both electrodes are able to reversibly insert and remove Li ions from their respective structures. On charging, Li ions are removed or deintercalated from the layered oxide compound and intercalated into the graphite layers. The process is reversed on discharge. The electrodes are separated by a nonaqueous electrolyte that transports Li ions between the electrodes. [Derived from (*4*)]

sizes combined with carbon-coating approaches to achieve core-shell morphologies has led to new directions in electrode materials (*14*). Reaction mechanisms and materials systems that were previously discarded are being reconsidered for the next generation of LIBs. Moving from bulk materials to nanosize particles has enabled (i) the ability to use new Li-reaction mechanisms, in which conversion-reaction electrodes show enormous capacity gains (*15*); (ii) the use of negative electrodes based on alloy reactions—Tin (Sn)–based LIB technologies have already reached the marketplace (such as NEXELION), and Si-based ones are emerging (*16*); (iii) the identification of poorly conducting polyanionic compounds or fluorine-based compounds that exhibit excellent electrochemical performance (*17*); and (iv) the transformation of the poorly conducting lithium iron phosphate ($LiFePO_4$) insertion electrode into perhaps the most valued electrode material for electric vehicle applications (*18*). LIBs based on $LiFePO_4$ are extremely attractive because of safety and cost. The former arises from the fact that the operating voltage of the $LiFePO_4$ system is compatible with the thermodynamic stability of the electrolyte, whereas the latter is based on the use of abundant and low-cost constituents. In addition to being an attractive LIB for the electric vehicle market, $LiFePO_4$-based batteries are being evaluated in stationary energy storage demonstration projects (*1*).

A substantial segment of the battery materials community is moving toward developing electrode materials on the basis of abundance and availability of the relevant chemicals. Materials centered on sustainable 3d metal redox elements such as manganese (Mn) [lithium-manganese oxide ($LiMn_2O_4$)], Fe ($LiFePO_4$, Li_2FeSiO_4) and titanium (Ti) (TiO_2, $Li_4Ti_5O_{12}$), and made via eco-efficient processes, are receiving increased attention (*19*). In addition, there is resurging interest in low-temperature–solution chemistry routes in which hydro(solvo)thermal, ionothermal, and bio-mineralization processes are used to prepare electrode materials at temperatures >500°C lower than traditional powder synthesis (*20*).

Life cycle costs represent another important consideration. A foreseeable strategy for battery processing will involve the use of electro-active organic electrode materials synthesized from "green chemistry" concepts through low-cost processes free of toxic solvents; this will also enlist the use of natural organic sources [carbon dioxide (CO_2)–harvesting entities] as precursors, which will be biodegradable and easily destroyed by combustion (providing CO_2) so that the battery assembly/recovery processes will have a minimal CO_2 footprint. Proof of this concept was demonstrated with the development of renewable organic electrodes belonging to the family of oxocarbons ($Li_2C_6O_6$) or carboxylates ($Li_2C_8H_4O_4$) and the assembly of the first eco-compatible LIB laboratory prototype (*21*). This work is extremely promising and suggests that the performance of organic electrodes could become comparable in gravimetric energy density, life cycle, and power rate to today's best inorganic electrodes, with the distinct advantage of providing a botanic alternative to the mineral approach currently in practice.

At the research level, there is interest in rechargeable LIB systems that have significantly higher energy densities (*22*, *23*). Although the $Li-O_2$ system has been available for many years as a primary battery, the prospect of developing it into a reversible (secondary) battery has become tantalizing because of a projected three- to fourfold increase in gravimetric energy density as compared with the current Li-ion technology (*24*). However, the volumetric energy density may not be much greater than that of Li-ion batteries (*25*).

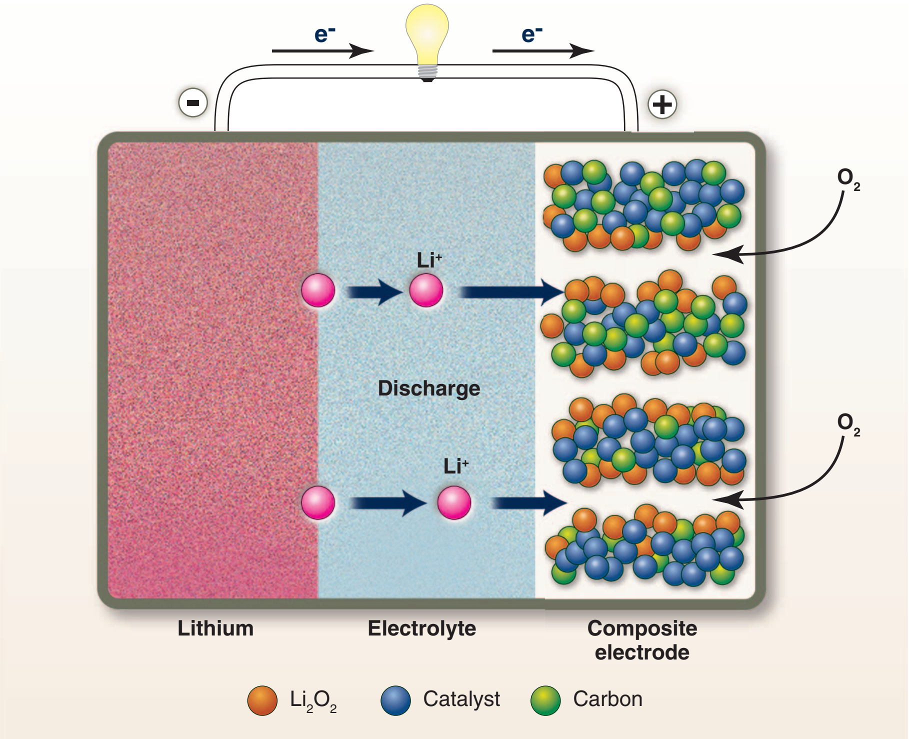

Fig. 4. The Li-air cell uses Li as the anode and a cathode consisting of a porous conductive composite, usually carbon and a catalyst, that is flooded with electrolyte. Oxygen from the atmosphere dissolves in the electrolyte and is reduced. On discharge, Li ions pass through the electrolyte and react with the reduced oxygen. The process is reversed on charging. Either aqueous or nonaqueous electrolytes can be used. For the former, a Li-ion–conducting solid electrolyte separates the metallic Li from the aqueous electrolyte.

The renewed interest in this system can be traced to the rechargeable behavior demonstrated in a nonaqueous $Li-O_2$ system (Fig. 4) (*26*). Although there has been considerable progress in the past 5 years in the area of electrode materials and architectures (*27*, *28*), a number of fundamental problems still need to be addressed, and it is difficult to anticipate which of the advanced $Li-O_2$ aqueous and/or $Li-O_2$ nonaqueous systems will be able to achieve capabilities beyond today's Li-ion batteries (*29*). Thus, there is little doubt that rechargeable Li-air cells either for electric vehicles or grid storage applications still have a long research and development path.

The prospect of developing Li-ion technology for both transportation and stationary storage raises the issue of whether the demand for lithium will affect the existing world reserves. Na is an attractive alternative because its intercalation chemistry is similar to that of Li, there are ample reserves, and its cost is low. These advantages are partially offset by the gravimetric energy density penalty for using Na, which is both heavier and less electropositive than Li. The development of room-temperature Na-ion cells that are cost-effective, sustainable, and environmentally benign will require a new generation of Na-intercalation compounds (*30*). The knowledge gained from developing Li-ion insertion electrodes should be applicable here. Thus, the demonstration of a viable Na-ion technology for stationary energy storage should come well before that of Li-air technology because of the accumulated experience with Li-ion technology and high-temperature Na battery technologies.

Sodium-Sulfur and Sodium-Metal Halide Batteries

High-temperature Na-based battery technologies can be traced back to the 1960s, when researchers

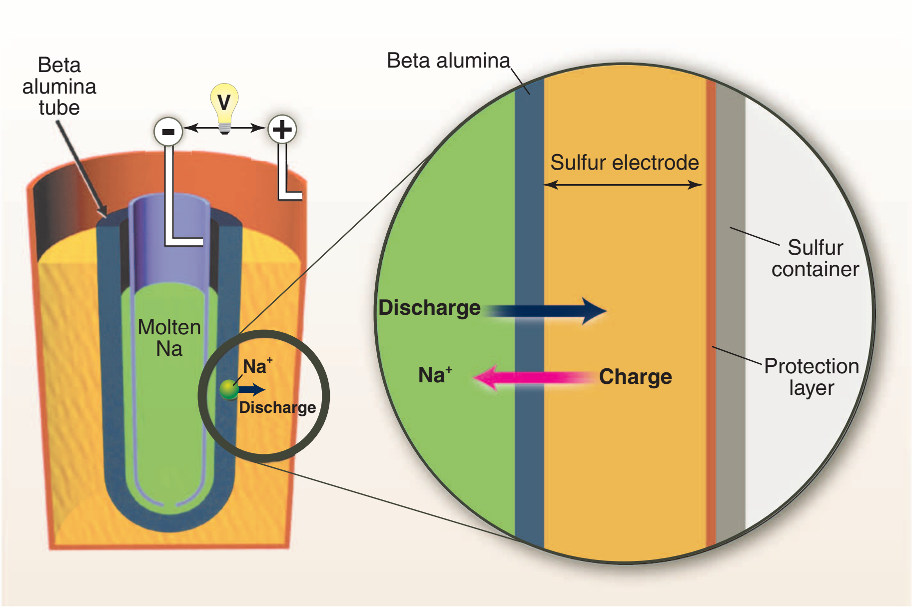

Fig. 5. Schematic of the Na/S battery. The central Na design has molten Na (negative electrode) contained within a Na β″-alumina solid electrolyte tube with molten S (positive electrode) surrounding the tube. The S electrode includes carbon in order to provide sufficient electronic conduction to carry out the electrochemical reactions. The magnified cross section of the cell shows the direction of Na^+ transport through the β″-alumina electrolyte. On discharge, Na combines with the S to form Na polysulfides. These reactions are reversed during charge, and Na returns to the interior of the tube.

at Ford discovered that a common ceramic refractory, sodium β-alumina ($NaAl_{11}O_{17}$), exhibited extremely high ionic conductivity for Na ions (*31*). At 300°C, the ionic conductivity for $NaAl_{11}O_{17}$ approaches that of the aqueous electrolyte, H_2SO_4, suggesting the possibility of using $NaAl_{11}O_{17}$ as a solid electrolyte in a high-temperature electrochemical cell. Although solids with high ionic conductivity had been known previously, none had β-alumina's combination of chemical and thermal stability and low electronic conductivity. The recognition that inorganic materials with high vacancy concentrations could exhibit "fast ion conduction"—many orders of magnitude greater than traditional alkali halides—led to the development of the field known as solid-state ionics.

The two high-temperature Na batteries, Na/S and Na-metal chloride (Na/$MeCl_2$), are based on using β-alumina as a Na^+-conducting membrane between two liquid electrodes (*32*). The batteries operate at temperatures of 270 to 350°C so as to take advantage of the increased conductivity of the β-alumina at elevated temperatures and ensure that the active electrode materials are molten. During discharge in the Na/S battery, Na is oxidized at the solid electrolyte interface, and the resulting Na^+ migrates through the electrolyte to react with S that is reduced at the positive electrode, forming Na_2S_5 (Fig. 5). Initially, a two-phase liquid is formed because Na_2S_5 is immiscible with S at these temperatures. Over half of the discharge occurs in the two-phase region, where the open-circuit voltage is 2.08 V (*33*). During charge, the Na polysulfides are oxidized, and when the Na content falls below Na_2S_5, the two phase-region of Na_2S_5 and S reappears. In this case, the formation of S must be managed appropriately, or else the S can deposit on or near the electrolyte, increasing cell resistance and limiting the amount of charging.

Early in its development in the 1980s, the Na/$MeCl_2$ battery was nicknamed the ZEBRA battery partially because of its scientific origins in South Africa, although its acronym stands for Zero-Emission Battery Research Activities. The positive electrode in this battery is a semisolid combination of an electrochemically active metal chloride such as $NiCl_2$ and a molten secondary electrolyte, $NaAlCl_4$, which conducts Na^+. During discharge, metallic Na is oxidized at the solid electrolyte interface. Na^+ ions are transported through the β-alumina electrolyte to the cathode via the molten $NaAlCl_4$. The solid metal chloride is converted into NaCl and the parent metal (Ni in the case of $NiCl_2$). The open-circuit voltage is 2.58 V (*34*). On charge, the Ni is oxidized, and the charge capacity is determined by the amount of NaCl available in the cathode.

Both batteries are based on the ion transport properties of the β-alumina family of materials. The high ionic conductivity of these materials is the result of an unusual structure in which "blocks" of closely packed Al-O are separated by "conduction planes" (*35*). The latter are loosely packed layers that contain the mobile Na^+ along with O^{2-} ions that bridge adjacent blocks. Ion motion occurs in two-dimensional honeycomb-like pathways around the bridging oxygen. The polycrystalline β″-alumina tubes used in the Na/S and Na/$MeCl_2$ batteries do not exhibit the anisotropic transport properties of single crystals because the fine-grained, randomly oriented microstructures effectively eliminate the anisotropy. Nonetheless, there are grain boundary and tortuosity effects so that the conductivity of single-crystal Na β″-alumina at 300°C, ~1 S cm^{-1}, is three to five times greater than the corresponding polycrystalline material (*32*). A recent study suggests that tortuosity effects can be diminished because Na β″-alumina electrolytes in a planar configuration exhibit higher ionic conductivity than that of tubular materials (*36*).

From inception, development for both systems targeted stationary energy storage and electric vehicles. As a result, the technologies share a number of common features (and challenges), even though specific designs differ somewhat. In both cases, the β″-alumina ceramic tubes are acknowledged to be the key element for determining battery operation and cost. Considerable development effort has gone into establishing large-scale manufacturing processes for automating the fabrication of high-quality ceramics with appropriate mechanical and electrical properties (*37*). Fracture of the ceramic is a vital concern because it leads to cell failure, whereas poor control of the ceramic microstructure results in interfacial reactions with the reactants. Large-scale production of β″-alumina has been established, but production yields and costs are major concerns (*38*). Other critical battery components are seals, which must not only be hermetic in the 300 to 350°C range but also withstand the vapor and/or actual contact with the highly reactive molten electrode materials. Recent activities in this area have involved the development of glass-ceramic sealing materials whose thermal expansion coefficient matches that of α- and β-alumina components (*39*). There is also the issue of identifying a low-cost material for containing the molten positive electrode. The corrosion problem is particularly difficult for Na/S batteries because both S and polysulfides are highly corrosive. The deposition of corrosion-resistant coatings such as carbides onto inexpensive substrates has proven successful (*40*).

Na/S battery technology has been commercialized in Japan since 2002, where it is largely used in utility-based load-leveling and peak-shaving applications. Among the advantages identified for stationary storage are its relatively small footprint (a result of high energy density), high coulombic efficiency, cycling flexibility, and low maintenance requirements (*41*). The production of megawatt-size energy storage batteries has involved considerable effort on such interrelated issues as electrical networking, cell reliability, thermal management, and safety (*42*).

To provide appropriate voltages, energy, and power, cells are assembled in series-parallel configurations to form modules, and the modules themselves are connected in series-parallel arrangements to form batteries. This networking approach is designed to minimize the effect of individual cell failures. Modules are thermally insulated and equipped with auxiliary heaters in order to maintain a minimum operating temperature. Thermal management is especially challenging. The internal temperature of a module increases on discharge because of joule heating and exothermic cell reactions, whereas during charge, there is a gradual cooling largely because of the cell endothermic reaction (*41*).

The Na/$MeCl_2$ batteries were developed almost exclusively for electric vehicles. At the time of their development, the technology seemed to offer certain advantages over Na/S in terms of tolerance to overcharge and overdischarge, the ability to assemble cells in the discharged state, a safe low-resistance failure mode, and potentially easier solutions for corrosion and sealing (*42*). Only recently have these batteries been directed at potential utility applications (*43*).

Redox-Flow Batteries

Redox-flow batteries also have their origins in the 1960s, with the development of the zinc/chlorine (Zn/Cl) hydrate battery. As a general description, a redox-flow cell uses two circulating soluble redox couples as electroactive species that are oxidized and reduced to store or deliver energy (*44*). By comparison, batteries rely on internal solid electrodes to store energy.

The flow-cell assembly (Fig. 6) has an ion-selective membrane separating the positive and negative redox species, which are contained in separate storage tanks. During operation, redox-active ions undergo oxidation or reduction reactions when they are in contact or close proximity to the current collector; the membrane allows the transport of non-reaction ions (such as H^+ and Na^+) to maintain electroneutrality and electrolyte balance.

Since the 1970s, numerous types of redox flow battery systems have been investigated (*45*). A partial list includes iron/chromium, vanadium/bromine, bromine/polysulfide, zinc-cerium, zinc/bromine (Zn/Br), and all-vanadium. The all-vanadium (1.26 V) and Zn/Br (1.85 V) systems are the most advanced and have reached the demonstration stage for stationary energy storage. Interest in the all-vanadium system is based on having a single cationic element so that the cross-over of vanadium ions through the membrane upon long-term cycling is less deleterious than with other chemistries (*46*).

Redox-flow batteries possess a number of advantages (*47*). The simplicity of the electrode reactions contrasts with those of many conventional batteries that involve, for example, phase transformations, electrolyte degradation, or electrode morphology changes. Perhaps their most attractive feature is that power and energy are uncoupled, a characteristic that many other electrochemical energy storage approaches do not have (*48*, *49*). This gives considerable design flexibility for stationary energy storage applications. The capacity can be increased by simply increasing either the size of the reservoirs holding the reactants or increasing the concentration of the electrolyte. In addition, the power of the system can be tuned by either (i) modifying the numbers of cells in the stacks, (ii) using bipolar electrodes, or (iii) connecting stacks in either parallel or series configurations. This provides modularity and flexible operation to the system.

Despite the apparent advantages for redox-flow batteries, application of this technology to stationary energy storage is still uncertain. One principal reason is that redox-flow systems have been limited to relatively few field trials. In contrast, other battery technologies have benefited from extensive experience in the development of products for portable electronics and automotive applications. A related disadvantage of flow batteries is the system requirements of pumps, sensors, reservoirs, and flow management (*48*, *49*). From a technical standpoint, there are reliability issues associated with the lack of appropriate membranes for controlling long-term ion cross-over effects. Designing better membranes is necessary, but whether such membranes can be of low cost is far from certain. Another important issue with redox-flow systems is that the currently used redox couples, even with enhanced solubility, are limited to concentrations of about 8 M. This feature is largely responsible for the fact that redox-flow systems do not surpass 25 Wh kg^{-1} (Fig. 2). The identification of lower-cost redox couples with high solubility would seem to be an essential development in order for this technology to succeed.

Researchers recognize that redox-flow approaches represent potentially new directions for increasing energy density. The semisolid Li battery demonstrated by Massachusetts Institute of Technology researchers uses electrode materials identical to those found in the LIB, but now the electrode materials are conducting inks (for example, suspensions of $LiCoO_2$ and of $Li_4Ti_5O_{12}$ powders in nonaqueous electrolyte solutions) rather than solids (*50*). The inks circulate separately on either side of a membrane that regulates the Li-ion transport between positive and negative electrodes. Both half cells and full cells have been demonstrated.

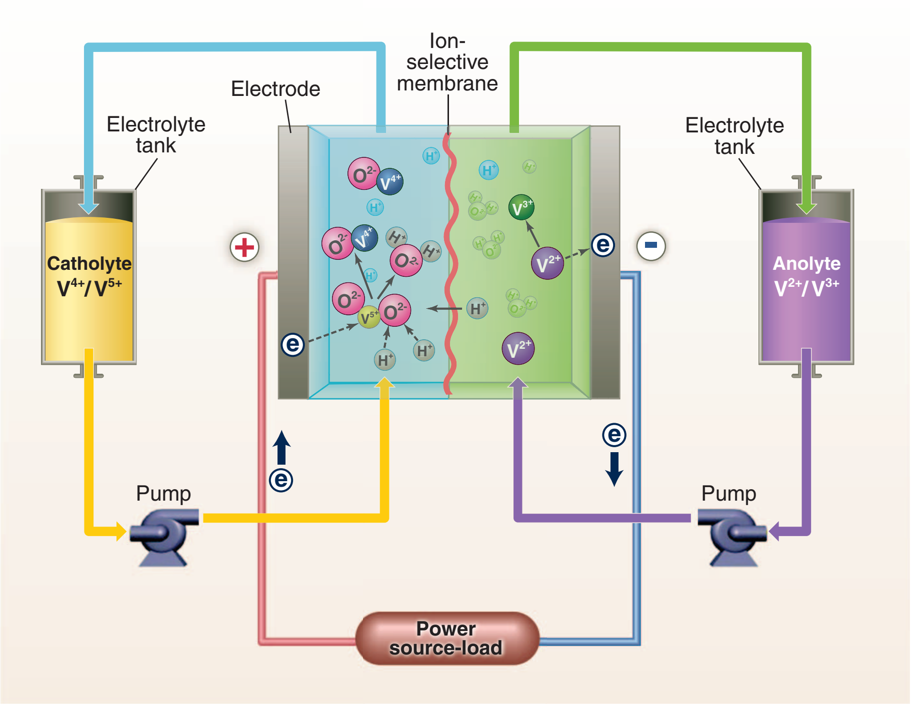

Fig. 6. Schematic of the various components for a redox-flow battery. The cell consists of two electrolyte flow compartments separated by an ion-selective membrane. The electrolyte solutions, which are pumped continuously from external tanks, contain soluble redox couples. The energy in redox-flow batteries is stored in the electrolyte, which is charged or discharged accordingly. In practice, individual cells are arranged in stacks by using bipolar electrodes. The power of the system is determined by the number of cells in the stack, whereas the energy is determined by the concentration and volume of electrolyte. In the vanadium redox-flow battery shown here, the $V^{(II)}/V^{(III)}$ redox couple circulates through the negative compartment (anolyte), whereas the $V^{(IV)}/V^{(V)}$ redox couple circulates through the positive compartment (catholyte). [Derived from (*38*)]

The novel feature here is the use of redox-active materials in suspension so as to circumvent the problem of the relatively low solubility of the metal ion redox couples in aqueous solution. The flowable inks will be in the 10 to 40 M range, which is at least 5 times higher than traditional redox flow systems. Combining the higher materials concentration with the feasibility of achieving 4-V working systems is likely to lead to considerable improvement in energy density, perhaps without substantially affecting power density.

Another Li-ion–based flow system was demonstrated recently by Goodenough and colleagues. In this design, an aqueous cathode operating in a flow-through mode was separated from a metallic Li anode by a Li-ion–conducting solid electrolyte and an organic liquid electrolyte (*51*). This redox-flow system used an aqueous cathode containing 0.1 M $K_3Fe(CN)_6$ and demonstrated highly efficient energy storage at 3.4 V. The design strategy presented here offers some noteworthy advances: (i) Li^+ ion transport in solution is enhanced as compared with that in a solid insertion cathode and (ii) the absence of structural changes during charge/discharge is beneficial for long-term cycling. The first laboratory prototypes were limited by low solubility of the metal-ion redox couple in the aqueous solvent and the poor mobility of Li^+ in the solid electrolyte. It is expected that the performance of the rechargeable alkali-ion cathode flow battery will improve substantially through the use of a better solid electrolyte and the possibility of using cathode inks. But perhaps the more important point illustrated in these studies is that redox-flow concepts adapt to other chemistries and hold considerable promise for improving battery performance and especially energy density.

Future Directions

There are two related questions that need to be addressed: What are the expectations for EES in the future, and what role will batteries play in this future? The first part is becoming clearer as the value of energy storage becomes increasingly evident. A recent EPRI study identified a number of high-value opportunities for energy storage, including wholesale energy services, integration of renewables, commercial and industrial power quality and reliability, transportable systems for transmission and distribution grid support and energy management (*1*). Moreover, some of these benefits are complementary, further improving the economics of energy storage.

The success of these applications of energy storage will depend on how well storage technologies can meet key expectations. The most important of these are low installed cost, high durability and reliability, long life, and high round-trip efficiency. The installed cost comprises the materials costs, production costs, and installation costs for the system. In the future, the preferred energy storage technologies will be composed of low-cost, easily acquired materials that are developed into products through a relatively simple manufacturing process and installed with few special requirements. Operations and maintenance costs are also important; these costs are often tied to the durability and lifetime of the energy storage solution, for which the lifetimes of most assets are measured in decades. Last, a premium will be placed on energy-efficient systems that do not lose energy through self-discharge or parasitic losses. With so many potential financial considerations, it is not surprising that cost is given as the reason that energy storage is not widely used on the grid.

The battery systems reviewed here satisfy several, but not all, of the energy storage criteria mentioned above. Na/S is commercially viable, and if this emerging technology follows patterns similar to others, costs can be expected to decrease as more production and operational experience is gained. The technology, which is more than 30 years old, needs to integrate some of the scientific advances that have taken place in the design of materials, creating new electrode architectures and identifying new chemistries to provide safe operation. Lowering the Na/S operating temperature is one topic that will affect the technology. Moreover, these advances will benefit Na-ion technology, which is of growing interest because of its promise as a low-cost approach for grid storage applications. Redox-flow batteries possess several promising attributes for energy storage, with low cost being one of the important drivers for this technology. A number of demonstration projects, ranging in size from 5 to 50 MWh and using a variety of different chemistries, are under way (*48*). The outcomes from these projects over the next 2 to 4 years will have a substantial influence on the future of this technology. The recent developments involving Li-redox flow and alkali-redox flow batteries stand as great opportunities that leverage existing knowledge of Li-ion batteries with the advantages of redox-flow systems.

Energy storage systems based on Li-ion batteries are expected to take a different route than either Na/S or redox-flow batteries. The development of Li-ion batteries for commercial electronics and automotive applications enabled this technology to address reliability, cycle life, safety, and other factors that are equally as important for stationary energy storage. The research environment for developing new low-cost materials is well established, and recent efforts directed at low-temperature processing and renewable organic electrodes provide the basis for future advances in the field. However, it is the volume production anticipated for the electric vehicle market that can lead to improvements in manufacturing process and provide an economy of scale that will bring about the lower costs required to make this battery technology viable for EES. Another interesting scenario is the prospect of recovering Li-ion batteries used in automotive industries and to give them a "second life" in large-scale energy storage applications.

Note added in proof: Na/S batteries were responsible for a fire that occurred at a power plant in Joso City (Ibaraki Prefecture) on 21 September 2011 (www.ngk.co.jp/english/news/2011/1028_01.html). Although the cause of the fire is still under investigation, this event underscores the fact that safety issues for Na/S batteries have not been completely resolved.

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Supporting Online Material
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Figs. S1 to S3
Table S1
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REVIEW

Lowering the Temperature of Solid Oxide Fuel Cells

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Fuel cells are uniquely capable of overcoming combustion efficiency limitations (e.g., the Carnot cycle). However, the linking of fuel cells (an energy conversion device) and hydrogen (an energy carrier) has emphasized investment in proton-exchange membrane fuel cells as part of a larger hydrogen economy and thus relegated fuel cells to a future technology. In contrast, solid oxide fuel cells are capable of operating on conventional fuels (as well as hydrogen) today. The main issue for solid oxide fuel cells is high operating temperature (about 800°C) and the resulting materials and cost limitations and operating complexities (e.g., thermal cycling). Recent solid oxide fuel cells results have demonstrated extremely high power densities of about 2 watts per square centimeter at 650°C along with flexible fueling, thus enabling higher efficiency within the current fuel infrastructure. Newly developed, high-conductivity electrolytes and nanostructured electrode designs provide a path for further performance improvement at much lower temperatures, down to ~350°C, thus providing opportunity to transform the way we convert and store energy.

Fuel cells are the most efficient means to directly convert stored chemical energy to usable electrical energy (an electrochemical reaction). Although the more common proton-exchange membrane fuel cells (PEMFCs) require hydrogen fueling, because they are based on proton conducting electrolytes, solid oxide fuel cells (SOFCs) can oxidize essentially any fuel, from hydrogen to hydrocarbons to even carbon, because the electrolyte transports an oxygen ion.

An SOFC consists of three major components: two porous electrodes (cathode and anode) separated by a solid oxygen ion (O^{2-}) conducting electrolyte (Fig. 1A). At the cathode, O_2 (from air) is reduced and the resulting O^{2-} ions are transported through the electrolyte lattice to the anode where they react with gaseous fuel, yielding heat, H_2O, and (in the case of hydrocarbon fuels) CO_2, and releasing e^- to the external circuit.

Multiple cells are combined in series via interconnects that provide both electrical contacts and gas channels between individual cells. The resulting "stacks" are then arranged in series and parallel configurations to provide desired voltage and power outputs from portable power and transportation applications, to distributed generation and large-scale power generation, in both civilian and military sectors (Fig. 1B).

Among the technologies available to convert hydrocarbon-based resources (which include not only fossil fuels but also, potentially, biomass and municipal solid waste) to electricity, SOFCs are unique in their potential efficiency. For stand-alone applications, SOFC chemical to electrical efficiency is 45 to 65%, based on the lower heating value (LHV) of the fuel (*1*), which is twice that of an internal combustion (IC) engine's ability to convert chemical energy to mechanical work (*2*). In a combined cycle, there are numerous combined heat and power (CHP) applications using SOFC systems, which have the potential to achieve efficiencies of >85% LHV (*3*).

Unfortunately, government policy, the popular press, and many scientific publications have focused on fuel cells as part of a broader hydrogen economy, thereby relegating fuel cells to a "future energy" solution due to the need for a required overhaul of our current hydrocarbon-fueling infrastructure. Although this may be true for PEMFCs, SOFCs have the advantage of fuel flexibility that allows them to be used on our existing hydrocarbon fuel infrastructure (*4*) while simultaneously providing efficiency gains (and corresponding CO_2 emission reductions).

Why Reduce SOFC Operating Temperature?

The key technical issue that has limited the development and deployment of this transformative technology is its high operating temperature, resulting in higher systems costs and performance degradation rates, as well as slow start-up and shutdown cycles, the latter dramatically limiting applicability in portable power and transportation markets. Over the past decade, considerable progress has been achieved in bringing the temperature down to an intermediate temperature (IT) range of 650 to 800°C so that metallic interconnects could be used to reduce cost.

Low-temperature (LT) SOFCs (≤650°C) can further reduce system cost due to wider material choices for interconnects and compressive nonglass/ceramic seals, as well as reduced balance of plant (BOP) costs. Moreover, below 600°C, both radiative heat transfer (Stefan-Boltzmann) and sintering rates exponentially drop off, thus reducing insulation costs and primary performance degradation mechanisms, respectively.

At even lower temperatures (≤350°C), cheap stamped stainless steel interconnects, elastomeric/polymeric seals (e.g., Kapton), and off-the-shelf BOP are possible. In addition, rapid start-up and repeated thermal cycling, from ambient to operating temperature, becomes possible. These are critical parameters for portable power and transportation applications, and it was because of PEMFCs' lower operating temperature (~100°C) that they were chosen for these applications over SOFCs, even though PEMFCs require hydrogen fueling.

Another reason to reduce operating temperature is maximum theoretical efficiency. In contrast to the Carnot cycle temperature dependence of IC engines, theoretical fuel cell efficiency increases with decreasing temperature [fig. S1 and supporting online material text (SOM text)]. For example, the maximum theoretical efficiency of an SOFC using CO as a fuel increases from 63% at 900°C to 81% at 350°C.

At first glance, this would imply that PEMFCs are more efficient than SOFCs because of their lower operating temperature. However, this ignores two important contributors to overall system efficiency. The first is that the vast majority of all H_2 produced today comes from hydrocarbon resources (typically CH_4), thus requiring additional external processes [e.g., steam reforming or catalytic partial oxidation (CPOX), water

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