Enabling Renewable Energy—and the Future Grid—with Advanced Electricity Storage

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Environmental concerns about using fossil fuels, and their resource constraints along with energy security concerns, have spurred great interest in generating electrical energy from renewable sources. The variable and stochastic nature of renewable sources, however, makes solar and wind power difficult to manage, especially at high levels of penetration. Electrical energy storage (EES) is necessary to effectively use intermittent renewable energy, enable its delivery, and improve the reliability, stability, and efficiency of the electrical grid. While EES has gained wide attention for hybrid and electrical vehicle needs, public awareness and understanding of the critical challenges in energy storage for renewable integration and the future grid is relatively lacking. This paper examines the benefits and challenges of EES, in particular electrochemical storage or battery technologies, and discusses the fundamental principles, economics, and feasibility of the storage technologies.

INTRODUCTION

Current annual worldwide energy consumption is estimated to be 15 TW (1 TW = 10^{12} watts).[1] Approximately 80% of today's energy is supplied from fossil fuels: oil (34%), coal (25%), and natural gas (21%).[2] Biomass is 8% of the energy supply, nuclear energy 6.5%, hydropower 2%, and other technologies such as wind and solar make up the rest. Even with aggressive conservation and development of new, higher-efficiency technologies, worldwide energy demand is predicted to double to 30 TW by 2050 and triple to 46 TW by the end of the century. Electricity will not only continue to be the dominant player (40% of all energy consumption in the United States in 2002), but its share will increase at a faster pace than overall energy consumption.[3] At the same time, oil and natural gas production is predicted to peak over the next few decades. Coal production accounts for about 40% of the electricity generated in the world;[4] abundant coal reserves may maintain current consumption levels longer than oil and gas. However, every kWh of electricity generated by burning coal co-produces an average 1,000 g/kWh life-cycle CO_2 emission, a greenhouse gas that is widely considered as the primary contributor to global warming.[5,6] In the United States, coal power plants emit 1.5 billion tons of CO_2 per year while emissions from developing countries are accelerating. While emitting fewer greenhouse gases, burning oil and natural gas results in a lifecycle CO_2 emission of 800 g/kWh and 400–500 g/kWh, respectively. To reduce greenhouse gas emissions, many countries are adopting tough regulations (i.e., cap-and-trade or variants) and carbon trading, which benefits industries with a small carbon footprint and requires those producing higher emissions to purchase carbon allowances.

The environmental concerns about fossil fuels and their constraints, combined with energy security concerns, have spurred great interest in generating electrical energy from renewable sources. Solar and wind energy are among the most abundant and potentially readily available.[5,7,8] The solar radiation energy the earth receives in one hour is enough to meet worldwide energy requirements for a year. Capturing a small percentage of potential wind energy could also contribute significantly to meeting the world's electrical energy requirements. While advancements in technology are still needed to harvest renewable energy economically, solar and wind power technologies have grown quickly. Globally, total installed wind power reached

How would you…

…describe the overall significance of this paper?

With increasing use of renewable power generated from intermittent sources such as solar and wind, interest has grown in research and development of stationary electrical storage. To help the materials community gain insight into the emerging area, this paper offers an overview on the needs, requirements, and potential technologies.

…describe this work to a materials science and engineering professional with no experience in your technical specialty?

A number of existing and emerging technologies are potential candidates for energy storage applications. All these technologies are, however, facing challenges to meet economic and performance targets for wide market penetration, which requires substantial advances in materials, design, system engineering, etc.

…describe this work to a layperson?

Batteries are widely used to store electrical energy for electronics and now hybrid vehicles. Can these batteries be used to store renewable energy? The answer may be yes. But they have to be capable of storing it at large scales and being cost-effective. Substantial advancement is required for the current battery technologies, along with non-electrochemical means, to meet the economic and performance targets.

74.3 GW in 2006 and 94 GW in 2007.[9] The World Energy Council estimates that new wind capacity worldwide will total up to 474 GW by 2020. The output from photovoltaic (PV) module installations increased to 2.5 GW by 2006 and is currently growing at 40% worldwide.[7] More countries and states are pushing for aggressive portfolios of renewable energy. In Denmark, penetration of wind power has already reached 17% of total power generation, and renewable generation will be doubled by 2015. In the United States, Hawaii has 20% of its electricity generated from wind and is gearing up for 70% to be generated from renewable sources by 2030. California is targeting 20% to be generated from non-hydro renewable sources by 2010 and no less than 33% by 2020. If hydro power is considered, California is at ~25% currently. The U.S. government has called for doubling the production of alternative energy in the next three years. Renewable energy is a centerpiece of the president's new economic plan to improve the U.S. economy.

However, solar and wind are not constant and reliable sources of power. The variable nature of these renewable sources makes any discussion of reliable instantaneous levels of solar or wind power moot. For example, as shown in Figure 1, wind power profiles in Tehachapi, California vary over minutes, hours, and days, while peaking at night when demand is low. During the day, wind power can be a few GW in some moments and only a few MW and even zero in others. Similarly, solar power is generated only in the daytime and varies when clouds pass by. Storage of electrical energy has been recommended as a way to eliminate this variability and adapt to the demand. Some view electrical energy storage (EES) as the "Achilles Heel of Renewable Energy."[10] Meanwhile, there has been intense discussion among the scientific community, renewable energy developers, and utility industries on the implementation and economic benefits of EES. Different scenarios are being considered. The most optimistic view is that renewable energy could be balanced out when integrated into a large electrical grid. The fast growth in renewable energy and aggressive renewable portfolio standards being set worldwide requires answering some fundamental questions: Can significant penetration of renewable energy be implemented without storage? If storage is indeed needed, what is the status of storage technologies relative to technical and cost targets; consequently, what research and development are needed to advance these technologies? In this paper, we attempt to answer these questions by discussing the need for electricity storage, examining the economic and technical status of potential storage technologies, and exploring fruitful directions for research and development.

THE NEED FOR ENERGY STORAGE IN THE FUTURE GRID

Energy storage is an established, valuable approach for improving the reliability and efficiency of electricity transmission and distribution (T&D). Sited at various T&D stages (Figure 2), storage can be employed to regulate frequency, control power quality, serve as reserve power, and provide load leveling or shifting.

Frequency is regulated using EES to balance generation and demand, which can fluctuate from second to second and minute to minute, to prevent disruptions that cost up to tens of billions of dollars annually in the United States alone. Electrical energy storage can also serve as reserve power to improve grid stability, for example, to avoid voltage collapse and a cascading outage or a blackout such as that which occurred August 11, 2003 in eastern Canada and the United States. Reserve power is important for internet and communication centers, which currently account for over 1.5% of the total utility power consumption in the United States, according to a report by Lawrence Berkeley National Laboratory. These digital communication centers are very sensitive to electricity fluctuation and disruptions. The most common applications of EES include improving the economics of power supply by load leveling or shifting, which involves storing electrical energy at one time and releasing it at another. Preferably, the energy is stored when excess is generated and released at times of greater demand. Load leveling is one kind of load shifting in which energy is stored when it can be produced cheaply (at off-peak times, for example) and released at peak times when it is more valuable.

To date, however, only 2.5% of the total electric power delivered in the United States passes through energy storage. That amount is primarily limited to applications associated with pumped hydroelectric storage. The percentages are higher in Europe and Japan, at 10% and 15%, respectively, largely because of favorable economics and government policies.[11]

Generally, existing grids that traditionally rely on base loads and are backed up by fossil-burning peak plants and spinning reserves, may handle some level of renewable. While their operating conditions may be acceptable, current grids face great challenges to reach significant levels of penetration with intermittent renewables and meet evolving changes in demand. However, there appears to be a critical limit over which the grid essentially becomes unreliable. The limits in percentage of renewable penetration reported so far range from 10% to over 30%, generally falling between 15 and 20%, depending on the size of the grid, renewable profiles, etc.[10] Reported by the Electric Power Research Institute, California, with penetration of wind power approaching 20%, the grid in Hawaii has already experienced instability.[10] One may argue that Denmark handles a 17% penetration of wind power without much use of storage. According to Incoteco, a Denmark-based energy consulting company, Denmark uses only 8–9% of the wind power generated. The rest is exported into Germany, Norway, and Sweden, which act as giant energy sponges with the help of some installed storage capacity. In anticipation of building another 4.5 GW offshore wind farm, Denmark is actively studying and evaluating suitable energy storage options.

An even greater challenge is that renewable sources are often localized and abundant in remote areas. With a great deal of wind or solar energy generation, sudden shifts in the local wind patterns or sunlight intensity can cause significant minute-to-minute imbalances between generation and load, resulting in changes in system frequency. A large change can trigger an automatic emergency shutdown of generation and cause a blackout. For example, on

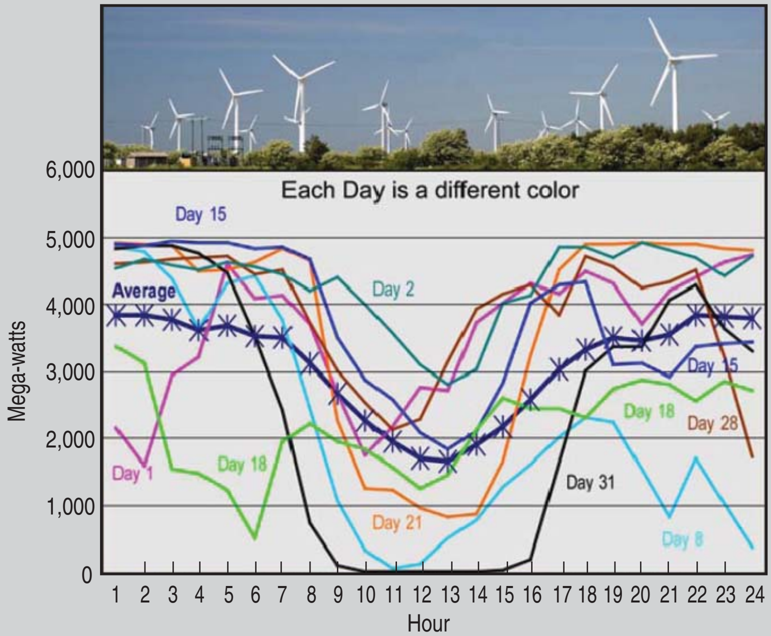

Figure 1. Daily profiles of wind power projected by 7x output in April 2005 for the year 2011 in Tehachapi, California. (Courtesy of ISO California.)

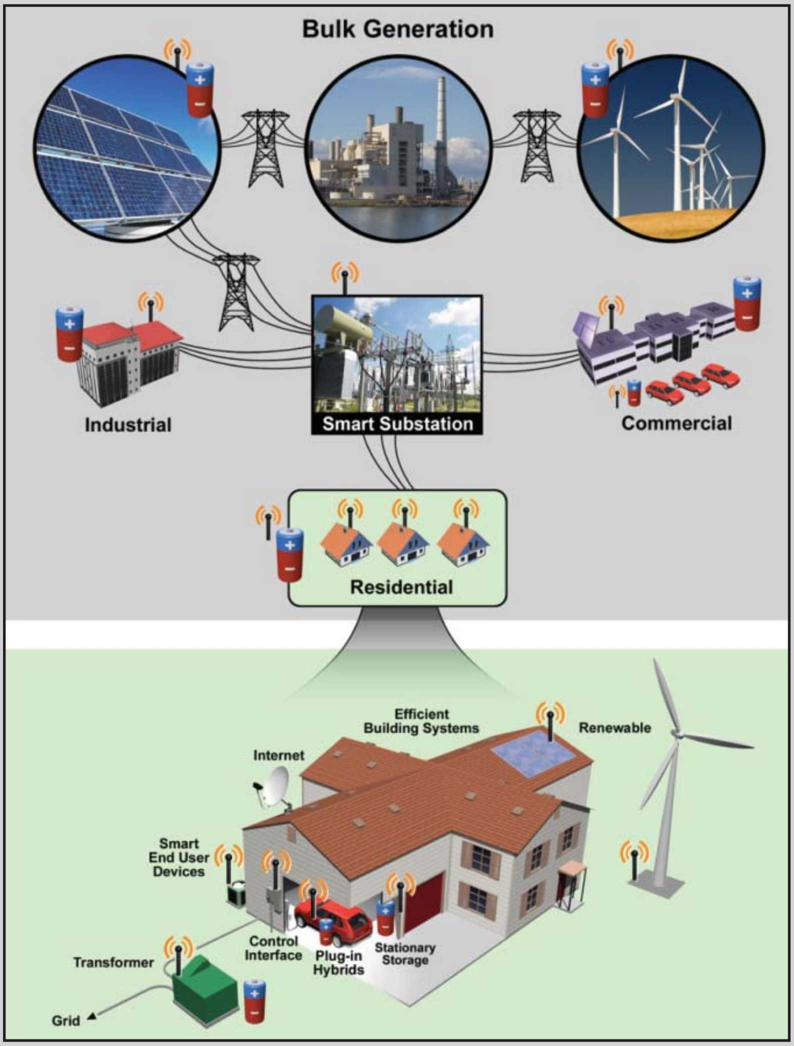

Figure 2. A schematic of applications of electricity storage for generation, transmission, distribution and end uses, and a future smart grid that integrates with intermittent renewables and plug-in hybrid vehicles through two-way digital communications between loads and generation or distribution grids.

February 27, 2008, a cold front moved through west Texas and winds died in the evening just as electricity demand was peaking. Generation from wind power in the region plummeted rapidly from 1.7 GW to only 300 MW. The sudden loss of wind power, and the lack of alternative electricity supply, forced grid operators to cut power to some offices and factories for several hours to prevent a statewide blackout. To ease the bottleneck limiting the development of wind resources in the state, it was proposed to build new transmission lines linking wind farms to customers. In addition to the high cost ($1.2–6 million per mile[12]), new transmission lines take a long time to build and negatively impact the environment by cutting through once-natural landscapes. The concerns over renewable transmission during the economic downturn shelved a plan to build the 4 GW Pampa Wind Form. Alternatively, integrating EES could help manage the variability in renewable electricity while reducing economic and environmental impacts. One of the important benefits of employing EES is indeed to allow for increasing penetration of renewables and deferring investment. Storage technologies become increasingly valuable with decentralized generation resources and users, a trend expected for the future "green" grid.[13]

Additionally, EES can be a valuable approach for improving the economics and utilization of renewable energy. Electrical energy storage can be sourced either at the generation site or close to loads (see Figure 2). If installed near a wind or PV farm, an EES system can store/release energy via load shifting in accordance with the generation profile. For wind power, this is called "firming and shaping" because it changes the power profile of the wind to allow greater control over dispatch. Similarly, when using EES with PV generation the extra electrical energy generated during daytime is stored for use at night when there is no power output. Load shifting helps improve the economy of renewable power and management of the balance between supply and demand. If pumped directly into electrical grids, intermittent renewable power is likely to disturb the balance between demand and supply.

A further incentive to employ EES is

that it can help reduce greenhouse gas emissions and enable the utility industry to meet anticipated carbon emissions limits. Without storage, renewable penetration would be backed up by fossil-burning turbines that run at low efficiencies and release greenhouse gases, mitigating the benefits of renewable energy. Based on a study by Carnegie Mellon

TECHNICAL AND ECONOMIC CONSIDERATIONS OF EES

Performance requirements of EES for stationary use depend on the application markets. For example, to regulate frequency, energy storage capacity may not need to be long-lasting—seconds or minutes are sufficient—but it must have a long cycle life because the system is likely to encounter multiple daily discharge events. High charge and discharge rates or high current densities are important although the state-of-charge of the storage system typically will not move over a wide range. In comparison, load shifting requires systems of up to MWh or even GWh levels that are capable of a high ratio of energy storage capacity to discharge power rating so that discharging can occur at a designated power for relatively longer periods, typically a few hours or more. For this type of application, high round-trip energy efficiency and a long deep-cycle life, along with low operation and maintenance costs are principal drivers. While storage for renewable power may cover the whole spectrum of discharging times, many agree this type of application demands technologies or systems that may range from a few kWh to MWh, and importantly, are capable of a long duration (hours) of storage. Unlike vehicle applications that have constraints on weight and volume, high-energy densities may not be strictly required for stationary applications. Also, the grid and renewable applications often require a quick response from the storage that can reach full power in a matter of a second. Finally, as utility assets, EES must have a long lifetime (e.g., >15 years).

Reliability/Safety of energy storage systems must be addressed for applications at scale due to the amount of stored energy. Many electric energy storage technologies, especially those that operate electrochemically, have the potential to release their energy rapidly if the structure fails or certain temperature limits are exceeded. The uncontrolled energy release can range from a thermal runaway event that simply drains the storage system of its energy to an explosive discharge of energy. Better safety and reliability requires the use of inherently safe materials/chemicals and better engineering of the storage systems against rapid, explosive releases of energy.

Cost is probably the most important and fundamental issue of energy storage, which can be expressed both in terms of the unit cost of power ($/kW) and the unit cost of energy capacity ($/kWh) or the per-cycle cost (¢/kWh). Unit cost of energy capacity better measures the capital cost for power management, while $/kW or ¢/kWh makes sense more for energy arbitrage. Different applications have different cost tolerances. Take load shifting and stationary renewable storage as an example. In the author's opinion, the cost of electricity storage probably needs to be comparable to the cost of generating electricity, such as from natural gas turbines at a cost as low as 4~5 ¢/kWh per cycle. Thus, to be competitive, the capital cost of storage technologies for energy applications should be comparable to or lower than $180~225/kWh, assuming a lifecycle of 15 years or 4,500 cycles (25 cycles per month). A capital cost of $800~1,100/kWh or less is desired if the technology can last 5 hours at the name-tag power. Unfortunately, most current technologies, except probably for pump-hydro (Figure A), cannot meet the economic requirement even without accounting for carrying charges, operation/maintenance (O&M), and replacement costs. There can be some room for renewable power generated at a higher cost than traditional natural gas turbines; but low cost is the primary driver for broad market penetration of storage technologies. Technologies capable of serving multiple markets, such as for both regulation and load-shifting, can be more competitive and are thus preferable to those serving a single function. Ultimately, cost reduction will rely on technology advancements to improve reliability, cycle life, efficiency, use of less expensive materials, etc.

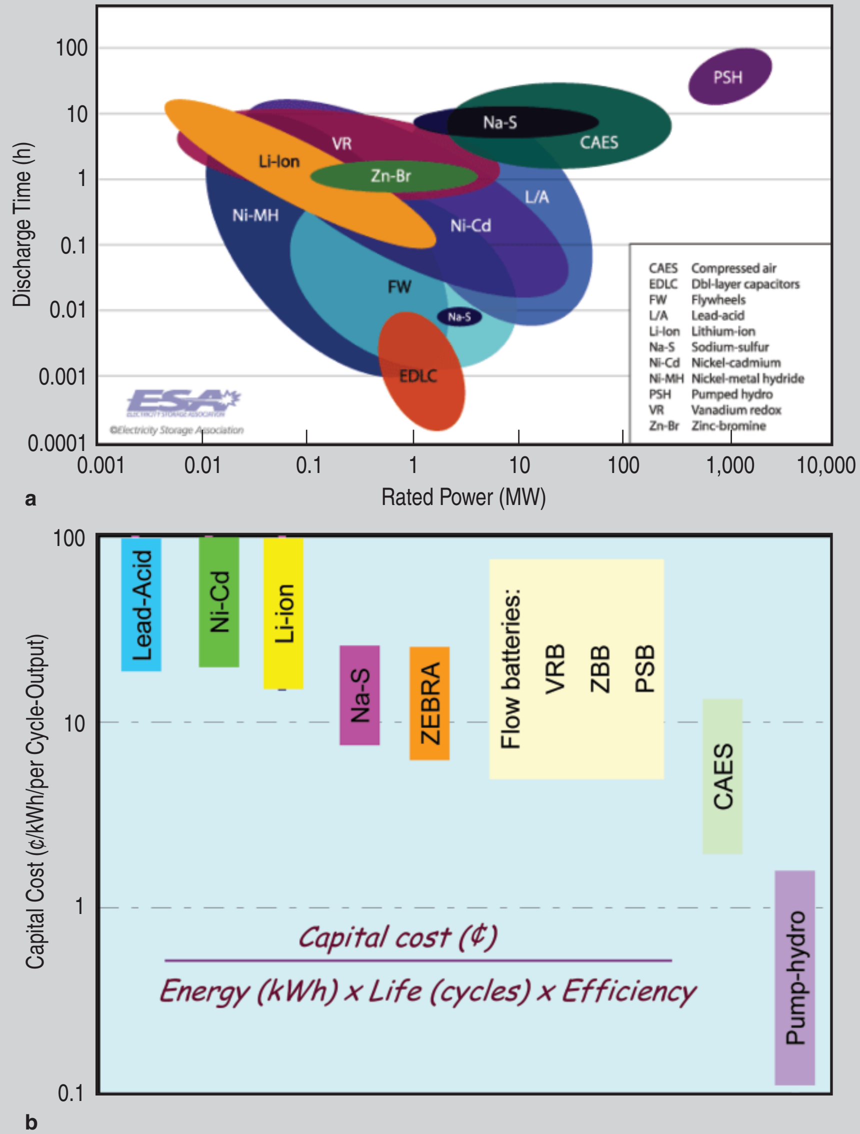

Figure A. A comparison of varied electrical storage technologies: (a) discharge time (hours) vs. power rating (MW); (b) approximation of capital cost per cycle. Note: carrying charges, O&M, and replacement costs are not included.[17,18]

University,[14] fossil back-up would penalize the reduction in CO_2 emissions from wind power by about 22% and the corresponding NOx saving by 70%. The U.S. Department of Energy (DOE) is targeting 20% wind penetration by 2030 or integrating approximately 300 GW of wind energy into the U.S. grid. Approximately 50 GW of peaking gas turbines would be used to compensate for the variability of the wind's power output.[15] Replacing gas turbines with electrical storage would greatly reduce greenhouse gas emissions.

Along with increasing integration of renewables, the future grid is expected to be able to provide fuel (i.e., electricity) to plug-in hybrid vehicles (PHEVs) and allow two-way communication and digital balancing of demand and supply (i.e., a smart grid). If most PHEVs are charged at night, wind energy that peaks at night may have a positive impact on the grids over time. However, adding solar power would shift the overall generation peak to daytime. The smart grid will be driven by the desire to improve capacity, which stands at about 40% in the United States, by shifting the demand curve through either incentives or controls. Electrical energy storage has been suggested as a key enabler for the future grid (Figure 2). The end-user storage system would store electricity from renewable generation or transmission line energy when it is cheap and charge vehicles or send electricity back to the grid during expensive peak hours. In addition, storage offers an effective alternative approach to help balance the system as a means to adapt production to demand while improving capacity. Given these benefits, and that deployment of EES may be more environmentally acceptable and potentially less detrimental to the economy and society than other types of upgrades, the U.S. Energy Independence and Security Act of 2007 authorized the DOE to develop and demonstrate storage technologies for utility applications.[16]

In short, high penetration of renewable energy and greater emphasis on energy efficiency, along with more electric vehicles and the use of smart grid technologies, is creating an urgent need for EES technologies that can ensure optimal and efficient use of generation, transmission, and distribution resources in a carbon-constrained world.

POTENTIAL TECHNOLOGIES: STATUS AND CHALLENGES

A number of technologies can be potential candidates and some of them were already demonstrated for renewable and utility applications. The storage characteristics, along with cost, are summarized in Figure A.[17,18] Electrical energy storage can be realized either by direct storage in electrical charges or by conversion of electrical energy into other forms of energy that may include chemical, potential, kinetic, etc. Direct storage technologies, such as electrochemical capacitors or supercapacitors, are highly efficient (close to 100%), but have low-energy density and discharge in seconds or sub-seconds. Thus, these technologies, along with storage in kinetic energy (i.e., flywheel) are useful for power management.

The electrical storage in potential energy, such as pump-hydro and possibly compressed air electrical storage (CAES), can be attractive options for bulk energy storage up to the GW level. With the lowest cost per cycle among the known technologies, a number of pump-hydro storage plants have been built and operated worldwide. Compressed air electrical storage plants use off-peak electricity to compress air into an air storage system. When the grid needs additional electrical power, air is withdrawn from the store, heated, and passed through an expansion turbine driving an electrical generator. There have been a few demonstrations including the municipal utility CAES plant being developed in Iowa. However, these two types of storage require a large initial investment, and more importantly, have geological and environmental limitations. Besides, the effectiveness and economy of CAES has not yet been fully proved, and the technology is not truly clean, consuming about 35% of the amount of premium fuel by a conventional combustion turbine (CT) and thus producing about 35% of the pollutants per kWh generated from a CT.

The largest group of technologies for stationary applications is probably electrochemical storage or batteries that can efficiently store electricity in chemicals and reversibly release it according to demand. Early technologies include lead-acid batteries that store and release electricity via a reversible electrochemical conversion of lead to lead sulfate at the anode and quadrivalent lead oxide to lead sulfate at the cathode in a concentrated sulfuric acid electrolyte. Over the last hundred years, lead-acid battery technology has been the most widely used of any electrochemical storage medium. These batteries have been applied to virtually every area of industry, and their sales constitute 40–45% of all battery sales in the world.[19] Since they are readily available, lead-acid batteries have been tested for utility applications, particularly for power regulation, power quality, and reliability control. The largest installation is a 40 MWh system built in 1988 in Chino, California that was used for load leveling at the Chino substation of the Southern California Edison Company. However, lead-acid batteries have a short cycle life and a high per-cycle capital cost (Figure A), in spite of the relative low energy cost in dollars per kWh. Interestingly, progress has been made lately by modifying the traditional lead-acid battery by the lead anode with active carbon, a material used in supercapacitors. Axion Power International, Inc. and East Penn of Pennsylvania are actively developing and demonstrating the technology for electrical grid applications. Evaluation at Sandia National Laboratory indicated a much improved cycle life over the traditional lead-acid batteries.

Other early technologies include varied nickel batteries that all share the same cathode (nickel oxyhydroxide in the charged state). In an aqueous KOH electrolyte, the cathode discharges to form nickel hydroxide. The anodes are either metals that oxidize to form a hydroxide or metal hydrides that lose hydrogen when discharged. Potential candidates for utility applications include nickel-cadmium, nickel-zinc, nickel-hydrogen, nickel-metal-hydride, etc. Among the most notable chemistry for utility applications are probably nickel-cadmium batteries.[11] This battery chemistry is characterized by a good energy density and excellent power delivery capability. A large system was commissioned in 2003 in Fairbanks, Alaska, to provide 27 MW_{ac} power for a short period of time (up to 15 minutes) until back-uo generation comes online. The battery system nevertheless uses toxic cadmium, which is a serious environmental hazard requiring special disposal. Also, it is susceptible to overcharge, and the direct-current-to-direct-current efficiency is only about 60~70%. The overall cost is still high (Figure A).

The high cost, technical concerns about electrochemical performance, and environmental hazards over the traditional technologies have spurred efforts to optimize technologies that were developed in the past few decades for the particular applications. These technologies may include, but are not limited to, redox flow batteries, sodium-oxide membrane batteries, some unique lithium-ion batteries, etc.

Flow Redox Batteries

Flow Redox Batteries (FRB) store electrical energy in two soluble redox fluids contained in external electrolyte tanks sized in accordance with application requirements (Figure 3). Aqueous liquid electrolytes are pumped from storage tanks to flow-through electrodes, where chemical energy is converted to electrical energy (discharge) or vice versa (charge). Between the anode and cathode compartments is a membrane that selectively allows cross-transport of non-active species (e.g., H^+, Na^+, etc.) to maintain electrical neutrality and electrolyte balance. Unlike traditional batteries that store energy in electrodes, FRB batteries are more like regenerative fuel cells in which the chemical energy in the incoming fuels is converted into electricity at the electrodes. As such the power and energy capacity of an FRB system can be designed separately. The power (kW) of the system is determined by the size of the electrodes and the number of cells in a stack, whereas the energy storage capacity (kWh) is determined by the concentration and volume of the electrolyte. Both energy and power can be easily adjusted for storage from a few hours to days or even weeks, depending on the application, which is another important advantage for the renewable integration. Generally, FRB sustains no damage to the cells when completely discharged, although overcharging may need to be avoided. There is only negligible self-discharge irreversible loss in optimized flow systems, and generally no problems associated with short circuiting. The liquid electrolyte and intimate interfaces with electrodes make high current densities and quick response (in a matter of sub-seconds) possible for utility applications. Simplicity in cell and stack structure allows for building large systems based on module design, which is another important advantage for electrical grid applications.

The foundational work on FRB was carried out at NASA in the early 1970s for space applications.[20,21] The early NASA FRB employed iron and chromium redox couples ($Fe^{2+}/Fe^{3+}||Cr^{2+}/Cr^{3+}$), both acidified with hydrochloric acid, giving an open circuit voltage of about 1.2 V. A critical issue with the early redox system was the permeation of iron species into the chromium electrolyte and vice versa, causing quick performance degradation. Interest in optimizing the Fe-Cr RFBs for grid applications has been renewed lately. To overcome the cross-transport issue, Maria Skyllas-Kazacos of the University of New South Wales, Australia, invented an all-vanadium redox battery (VRB) in the mid 1980s.[22,23] Unlike the chromium-iron cell, VRBs use the same element, vanadium, in the sulfuric-solution anolyte and catholyte. The energy conversions in the battery are realized via changes in vanadium valence states through the following electrode reactions:

$$VO^{2+} + H_2O + V^{3+} \underset{Discharge}{\overset{Charge}{\rightleftharpoons}} VO_2^+ + 2H^+ + V^{2+}$$

$$E^o = 1.26V \quad (1)$$

The overall electrochemical reaction gives a standard cell voltage of 1.26 V (at 1M and at 25°C). The chemical stability of the sulfuric electrolytes, however, limits the all-vanadium operation to the 10–40°C range, with an energy density about 25 $Wh.kg^{-1}$.[24]

In RFB's acidic environment, inert, high-surface-area carbon or graphite-based materials in forms such as felt or porous structure were often bonded with a conductive substrate such as a conductive polymer as a current collector to form electrodes.[25–27] The fast kinetics of the vanadium redox reactions allows high columbic and voltaic efficiencies often without the use of expensive catalysts.[28] Perflorinated sulfonic acid membranes (e.g., Nafion membranes) generally have been used due to their high ionic conductivity (0.07~0.23 Scm^{-1} for H^+) and good chemical stability in the electrolytes.[29–30] Recent studies attempted to modify the Nafion membranes for improved permeability and selectivity as well as chemical compatibility with V^{5+} electrolytes.[31–33] Up to 92% cell efficiency and 80% from 10 KW have been reported.[34,35]

The first large VRB (50 KW/200 kWh) was built by Kashima-Kita Electric Power, a Mitsubishi subsidiary, and went into operation in 1995. Since then systems up to MWh levels were developed and demonstrated. In 2005, Sumitomo Electric Industries successfully demonstrated a 4.0-MW/6.0-MWh system at the 32-MW Tomamae wind farm on Hokkaido in northern Japan. A cycle life of >6,000 cycles (80% depth of discharge) and a calendar life up to 8 years (longer with replacement of components) has been demonstrated for small systems.[21]

In addition to the aforementioned, a number of other flow battery chemistries have been studied or developed.[20] Among them are polysulfide-bromide (PSB) and zinc-bromide batteries (ZBB). Figure 3 depicts electrochemical reactions of these two RFBs. The PSB systems employ electrolytes of sodium bromides and sodium polysulfides.[11,21,36] The electrolyte solutions are separated by a selective membrane to prevent the sulfur anions from reacting directly with the bromine, and the electrical balance is achieved by the transport of Na^+ across the membrane.[21] Polysulfide-bromide systems with ratings from kWh to MWh were developed by Regenesys Technologies Ltd., a wholly own company of Innogy UK (later bought by VRB, Inc. and since sold to Prudence Energy). In ZBB, the electrolyte is an aqueous solution of zinc bromides plus agents.[37,38] During operation, the electrolyte is pumped through positive and negative electrode surfaces separated by a microporous plastic film, or alternatively, an ionic membrane that selectively allows the transport of zinc and bromide but not the aqueous bromine, polybromide ions, or complex phase. Since zinc is reversibly deposited from the ions at the anode, ZBB are not truly redox batteries and thus often referred as a "hybrid" RFB. In the mid-1980s, Exxon licensed the technology to a number of companies that included Johnson Controls, JIC, who in 1994 sold their interest to ZBB Energy Corporation. Since then, ZBB has developed 50-kWh and 500-kWh systems based on a 50-kWh battery module. Meidisha, another company that licensed Exxon's technology, demonstrated a 1-MW/4-MWh ZBB battery in 1991 at Kyushu Electric Power Company in Japan.[11]

One advantage of PSB and ZBB is the use of the abundant, low-cost chemicals. These two batteries have a higher voltage than VRB and potential higher energy densities. But their cycle-life, efficiency, and reliability may be inferior to VRB. In addition, the formation of zinc dendrites upon deposition and the high solubility of bromine in the aqueous zinc bromide electrolyte has hindered the ZBB development.[19] Its self-discharge rate is also higher than VRB and PSB.

With all the stated advantages and the successful demonstration of systems up to MWh levels, none of the RFB technologies have seen broad market penetration. First and foremost, the current technologies are still expensive. Advances in science and technology continue to bring down the cost; VRB, for example, is about \$500/kWh or higher,[39] which is about two–three times higher than the target expected for broad market penetration. The high cost is directly dependant on the high cost of materials/components and performance parameters including reliability, cycle/calendar life, energy efficiency, system energy capacity, etc.

Sodium (Na)-solid Oxide Membrane Batteries

Sodium-solid oxide membrane batteries (SBB) reversibly charge and discharge electricity via an Na^+ conducting solid oxide membrane. A notable and the most mature membrane is β''-Al_2O_3 stabilized with Li_2O or MgO that demonstrates an excellent ionic conductivity.[40] To achieve a satisfactory performance, SBB operate at moderate temperatures (300–350°C) using liquid sodium as anodes. The most common cathode comprises molten S/Na_2S_x, which adds porous graphite felts to improve its electron conductivity. This type of battery is known as a sodium-sulfur (Na-S) battery. Alternatively the sulfur cathode is replaced by porous $Ni/NiCl_2$ structures impregnated with molten $NaAlCl_4$ in ZEBRA batteries. Both Na-S and ZEBRA are traditionally built in tubular designs, as schematically shown in Figure 4, which also depicts their electrochemical reactions.

The Na-S battery was initially developed by the Ford Motor Company in the late 1960s and 1970s for electrical vehicle applications, and halted in the mid-1990s with the emergence of battery technologies such as nickel-metal hydride and later lithium-ion. By the early 1980s, the Tokyo Electric Power Company collaborated with NGK Insulator, Inc. to develop Na-S technologies for utility energy storage. By the late 1990s, varied systems up to the MWh scale had been developed. A number of MWh systems have been demonstrated on the electrical grid. The largest system currently under construction is a 34-MW/238-MWh (7 hours) Na-S storage for the Rokkasho wind farm in northern Japan.

One major advantage of the Na-S battery is its high energy efficiency (up to over 90%), due in part to its nearly 100% columbic efficiency. The Na-S battery demonstrates an energy density comparable to some lithium-ion chemistries. In addition, the molten electrodes in the battery ensure a high current density and a quick response to changing power conditions. A calendar life of up to 15 years and a cycle life of 4,500 cycles with 90% depth of discharge have been achieved. However, operation at elevated temperatures requires an effective enclosure and/or stringent thermal management to maintain energy efficiency and provide adequate stand time. There is also the need to improve safety, durability, reliability, etc. Molten sulfur is not a good conductor and corrosive to the container. A structural breakdown of the oxide electrolyte would lead to direct contact of molten sulfur and sodium, resulting in fire or potential catastrophic failure. During off-times, the system must be maintained at elevated

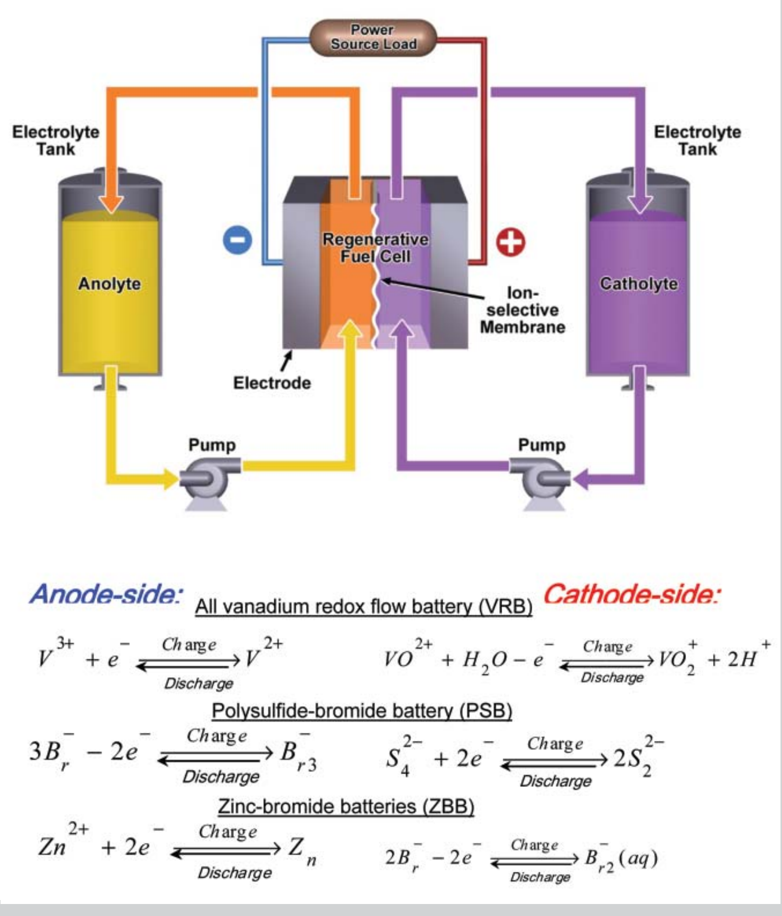

Figure 3. A schematic of a redox flow battery and selected redox chemistries.

temperatures. Freezing cycles induce mechanical stress, potentially causing structural failure often after only a few cycles. The cost is still too high for broad market penetration, although technology advancement and scaled production have reduced it.

In ZEBRA or Na-$NiCl_2$ batteries, sodium ions are transported through the oxide membrane from the anode to the cathode during discharge, reducing $NiCl_2$ to Ni via migration of sodium ions in $NaAlCl_4$. The concept of ZEBRA was proposed in 1978 and further developed by BETA Research and Development Ltd. in England.[41,42] MES-DEA acquired the ZEBRA technology and has since been involved in commercialization efforts. Recently FIAMM and MES-DEA formed a new company, FZ Sonick SA, to further develop the technology. The use of solid or semi-solid cathodes makes Na-$NiCl_2$ batteries intrinsically safer and less corrosive than Na-S batteries. The high voltage of Na-$NiCl_2$ batteries helps energy density. Nevertheless, there is need of further improvement in power, reliability, etc. Recently General Electric developed the Na-$NiCl_2$ batteries and built a factory in New York. Under support by the DOE ARPA-E Program, Eaglepicher is teaming up with Pacific Northwest National Laboratory in developing the planar design of the Na-$NiCl_2$ chemistry.

Lithium-ion Batteries

Lithium-ion batteries store electrical energy in electrodes made of lithium-intercalation (or insertion) compounds (Figure 5). During charge and discharge, Li^+ ions simply transfer across a liquid organic electrolyte between one host structure and the other, with concomitant oxidation and reduction processes occurring at the two electrodes. The lithium-ion technologies started with discovery of intercalation compounds such as Li_xMO_2 (M=Co, Ni, Mn) that were initially proposed by Goodenough and are still widely used today.[43,44] The finding of highly reversible, low-voltage lithium-intercalation carbonaceous materials led to the commercialization of $Li_xC_6/Li_{1-x}CoO_2$ rocking-chair cells by Sony in 1991.[45,46] The lithium-ion cells operate around 4 V and demonstrate a capacity and power about 150 Ah·kg^{-1} and over 200 Wh·kg^{-1}, respectively.[46] The favorable electrochemical performance in energy and power densities and advancement in system design and manufacturing made the early lithium-ion a great success for mobile electronic applications in spite of remaining challenges. Among these is that the early lithium-ion chemistries are inherently unsafe. The lithiated-graphite electrode operates at a potential close to that of metallic lithium, leading to lithium-dendrite growth and potential electrical shorting. In the presence of flammable organic electrolyte solvents currently in use, there is a risk of heat generation, thermal runaway, and fire. An additional challenge is the high cost that may not be critical to electronic applications, but is very important for scaled-up vehicle applications, which so far consider lithium-ion as the most promising technologies.

In the past decade or so, substantial progress has been made in advancing the lithium-ion technologies, mainly driven by broad interests and extensive efforts for hybrid, plug-in hybrid, and electrical vehicles. For high-energy

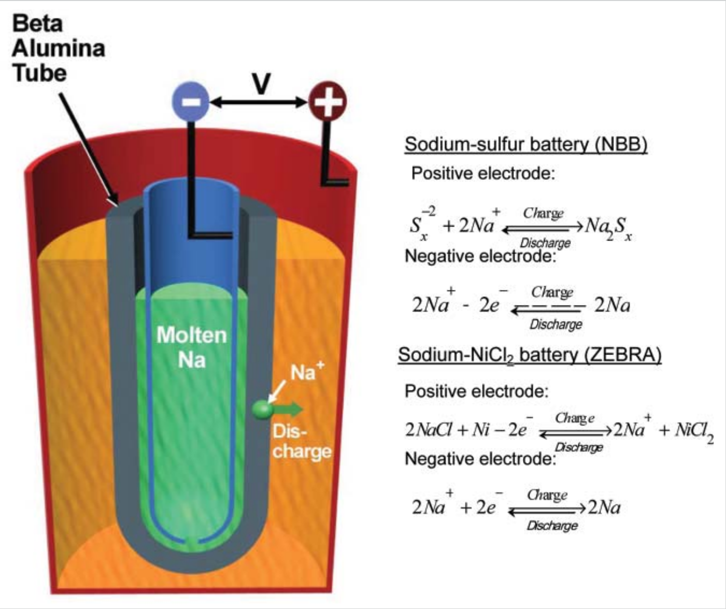

Figure 4. Single-cell and tubular design of a sodium-beta battery and electrode reactions.

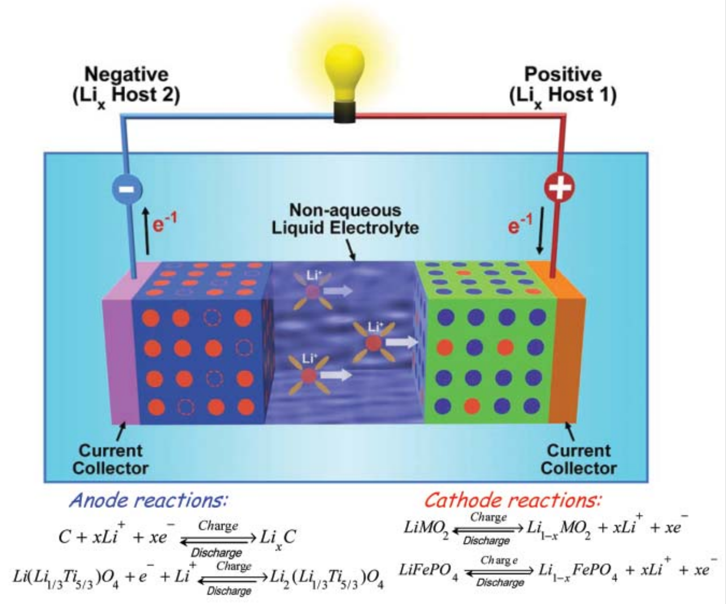

Figure 5. A schematic of a lithium-ion battery cell in which, during discharge, Li^+ ions migrate through the electrolyte and electrons flow through the external circuit, both moving from the anode (– electrode) to the cathode (+ electrode), along with selected electrode reactions.

capacity, alloys and/or intermetallics have been extensively investigated as negative electrodes. While promising progress has been made with the high-capacity alloy anodes, structural stability issues remain that are ascribed to large-volume expansion during alloying with lithium.[46,47] Metal oxides, especially lithium titanate spinel $Li_4Ti_5O_{12}$, have been found as safe alternatives to the graphite anode.[48–50] The titanate anode operates at 1.55 V vs. Li^+/Li and can accommodate lithium with a theoretical capacity of 175 $mAh \cdot g^{-1}$. While sacrificing energy density to some extent, the relatively high potential versus lithium makes titanate electrodes intrinsically safer than graphite. In the titanite spinel, the $\{Li_{1/3}Ti_{5/3}\}O_4$ framework provides a three-dimensional network of channels for facile Li^+ diffusion and exhibits little or no volume expansion even during lithiation. Accordingly, good reversibility and the ability to resist structural change during lithium insertion/extraction make it an attractive anode for applications that require a long cycling life. There are no, or few, side reactions with electrolytes directly related to the irreversible capacity and power loss. This allows for the use of nanostructures to improve rate capability, and thus power, without side reactions with electrolytes. The good chemical compatibility, along with the relative high potential vs. Li^+/Li make the titanite anode much safer than the carbon-base ones. In addition to lithium titanates, varied TiO_2 polymorphs including TiO_2-B, anatase, rutile, etc. have been found as an active lithium host, and some of their nanostructures have demonstrated promising electrochemical properties.[51–54]

On the positive electrodes, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ was developed as an alternative to the $LiCoO_2$ cathode.[55–57] In addition to lower cost, the former demonstrates higher capacity, longer cyclability, and better safety compared to $LiCoO_2$. Other alternatives include $LiMn_2O_4$ (spinel) and its derivatives that have a voltage of over 4.0 V versus lithium and a capacity about 10% less than that of $LiCoO_2$. Although much more cost-effective than $LiCoO_2$, the spinels have a tendency to dissolve in electrolyte and undergo Jahn–Teller-driven cubic-tetragonal structural distortion during deep discharge, which degrades battery performance and reduces battery life.[46,58] In the late 1990s, Padhi et al. proposed $LiFePO_4$, which exhibits a lower voltage (~3.5V vs. lithium), but a higher capacity of 170 mAh/g in comparison to $LiCoO_2$.[59] In addition to its low cost and being environmentally benign, the olivine structure is highly stable and allows for long cycles of Li-intercalation/deintercalation. However, the material exhibits low lithium-ion and electronic conductivity. Introducing nanostructuring, carbon coatings, and doping shortens the lithium-diffusion distance and enhances electron conduction, substantially improving the performance of the olivine structured chemistry as cathodes.[60–63] Nanostructured $LiFeO_4$ has gained commercial success in the lithium-ion batteries.

Given the high energy/power density and nearly 100% energy efficiency and anticipated mass production, lithium-ion technologies are considered valuable storage options for renewable end users, and distributed grids. There has been discussion on the use of the lithium-ion battery stacks after their life service on hybrid or electrical vehicles. This would extend the values of the batteries that are initially developed for the transportation applications. It remains questionable, however, if the after-use batteries can meet the performance and economic matrix for stationary applications.

Alternatively, there are increasing incentives and the need to develop lithium-ion batteries specifically for stationary applications. This becomes particularly important, given the difference in requirements between stationary and transportation applications and the fact that, currently, no lithium-ion chemistry meets the performance and economic matrixes for both applications. The lithium-ion technologies for the stationary applications should focus on cost-effective chemistries or materials that provide long calendar and cycle life. Particular interest would be on electrode materials and electrolytes that are structurally stable and chemically compatible during lithium insertion/deinsertion. Altairnano developed a lithium-ion battery based on nano-titanite anodes and demonstrated up to 2.0 MW systems. Operating with a relatively lower voltage (2.3V) and of a lower energy density than conventional lithium-ion chemistries, the Altairnano technology offered a great range of safety (–40–260°C), long calendar and cycle life (>15 years and >10,000 cycles), and high power (4 $kW \cdot kg^{-1}$). The system demonstrated a quick response, in a matter of milliseconds, to control commands and a round-trip efficiency of about 90%. However, it could only last up to 15 minutes at the name-tag power. A123 developed a lithium-ion battery based on nanostructured $LiFePO_4$ cathode and demonstrated up to 2.0 MW systems for power management. Similarly, the A123 system lasted only 15 minutes at the name power. Heat management appears among major challenges for better technologies. Overall, lithium-ion technologies have not yet been fully demonstrated to meet the performance and economic matrix for the utility sector. Further investment and efforts are needed to develop suitable lithium-ion technologies that can support increasing penetration of renewable energy and stabilizing of the electrical grid. Significant advancements are needed in materials, processing, design, and system integration for the technologies to achieve broad market penetration.

CONCLUSION

The current trend toward reducing greenhouse gas emission and increasing penetration of renewable energy, along with increasing demands of high-quality power, calls for urgent development and implementation of EES. Without suitable EES, the current electrical grid could allow for only a limited level of penetration of renewable energy generated from intermittent sources such as wind and solar. Over-penetration would destabilize the grid, potentially causing shutdowns and even blackouts. Further challenging is that intermittent renewable sources are typically rich in certain areas, which are often far away from load centers. Installing EES into the grid would not only facilitate increasing penetration of renewables, but ensure quality power for a society becoming increasingly digitized. Implementing EES would help reduce greenhouse gas emissions by replacing fossil-burning turbines currently employed to stabilize the grid. Energy storage can be a key enabler for a future grid that integrates extensive renewable generation and provides power for plug-in vehicles. Detailed studies on effective and economically viable use of EES in the future grid are needed.

A number of potential technologies for EES exist, and some of these have been demonstrated for utility applications. However, these technologies are facing either challenges in meeting the performance and economic matrix for the stationary applications, or limits in environment, site selection, etc. This calls for both basic and applied research to further develop current technologies and to discover new technologies that can address the needs for renewable and utility applications.

Currently, only limited R&D have been performed in advanced storage technologies for utility and renewable applications. This is particularly true compared to storage technology research and development for vehicle applications. Unfortunately, there are only a few government-funded programs worldwide for developing electricity storage technologies for stationary applications. There is a general public and political lack of awareness of the need for new technology for these applications. Even renewable energy industries are reluctant to lend support due to concerns about adding extra cost to renewable power systems as they struggle to reduce system cost. Lately, however, there appear signs that the current trend is reversing. Along with the electrical storage for vehicle applications, development and demonstrations of large-scale storage technologies have been proposed in the American Recovery and Reinvestment Act of 2009. A number of other countries have also shown increasing interest in stationary storage research and development, suggesting a bright outlook for development of stationary energy storage technology for the future electric grid.

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