

Scope: This article provides insights into the trade-offs among performance parameters affecting battery cost that are now driving the research frontier of battery storage. For the full set of articles as well as information about the contributing authors, please visit <http://acee.princeton.edu/distillates>.

# Article 4: The Technological Frontier of Electrochemical Energy Storage

The designer of a battery for grid-scale storage aspires to achieve fast discharge, a long cycle life, high efficiency, and low-cost capacity. It is not inconceivable that a storage system can be fully discharged in seconds, can cycle reliably thousands of times, can achieve nearly 100 percent round-trip efficiency, and can meet a target for the installed cost of storage capacity like \$100/kWh. However, today, no single technology meets all of these goals, and few meet even one of these goals. In order to gain an appreciation of the research frontier for battery storage, we explore here the characteristics of three popular battery chemistries: lead-acid chemistry, lithium-ion chemistry, and sodium-sulfur chemistry. These by no means span all possibilities, but when considered as a group they provide insight into the balancing of objectives that one must consider at the frontier of electrochemical energy storage.

The discussion below focuses on the differences between cells based on these chemistries, but it is important to keep in mind what these cells and many others have in common. Foremost, all of these electrochemical cells promote a reversible reaction between a reduced and an oxidized species, while generating or absorbing energy depending on the direction of the reaction. All cells generate heat in both charge and discharge mode, due to electric-resistance-based losses (Ohmic losses) during operation, and therefore cells based on these chemistries must be designed with heat management in mind. All cells must also contend with unwanted (“parasitic”) side reactions, due to both innate chemistry and interactions with their environment. The parasitic reactions, if left unchecked, can further reduce roundtrip efficiency, and if these side reactions are irreversible they will limit the ultimate cycle life and shelf life of the cell.

**Lead-acid chemistry** is the basis of the oldest and most ubiquitous battery storage system. Conventional car batteries are typical lead-acid batteries. The lead-acid battery consists of a lead anode, a lead oxide cathode, and an aqueous electrolyte (typically, sulfuric acid). Other water-stable cells include the alkaline batteries (zinc nickel, nickel cadmium, and others), aqueous flow

cells (vanadium redox, hydrogen bromide, zinc bromide, and others), and the more recent sodium ion systems. The nomenclature is confusing in this respect: the well-known “dry” alkaline cell is an aqueous cell, with massive water content compared to the non-aqueous cells discussed below. It is called a dry cell because the caustic electrolyte is present in gel form and will not “leak” when punctured. Aqueous systems are the easiest to manufacture and scale up.

However, water brings problems. The lead-acid system, like other aqueous systems, must contend with damaging water-based parasitic side reactions that restrict their operating cell potential (voltage), notably the electrolysis of water, which produces hydrogen gas. The generation of hydrogen promotes self-discharge, which limits long-term stability, shelf life, and round-trip efficiency. The generation of hydrogen also presents a risk of fire. Electrolysis occurs at the relatively low voltage of 1.23 volts, and therefore, in theory, to prevent hydrogen production 1.23 volts should be the maximum allowed cell potential. In fact, for some systems, due to the sluggish kinetics of water-splitting, active and passive gas management systems can mitigate or eliminate the unwanted electrolysis side reaction until a voltage as high as 2.2 volts is reached. The deleterious effects of electrolysis are the main constraint on aqueous storage systems.

Maximum power, self-discharge, and shelf life vary with temperature, and the battery’s range of operating temperatures is determined by the boiling point and freezing point of the water-based electrolyte. The range of operating temperatures is wider than that of pure water, because the electrolytes tend to be concentrated salt solutions.

**Lithium-ion chemistry** represents the pinnacle for batteries of energy density (deliverable energy divided by mass) and power density (deliverable power divided by mass), and as a result batteries based upon this chemistry dominate the portable electronics market. These cells operate reversibly at a cell potential as high as three to four volts,

which requires that the concentrations of both oxygen and water be restricted to less than one part per million. The need to exclude water requires non-aqueous electrolytes today. Typically, the electrolyte is a volatile organic compound, but solid-state electrolytes and ionic liquids with reduced flammability are under investigation. The exclusion of oxygen and water increases the manufacturing and materials cost of lithium-ion batteries compared to aqueous cells. Lithium chemistry is inherently less safe than aqueous chemistries because of the higher voltage and (at least at present) the flammability of the volatile electrolyte.

Due to the reactivity of lithium, parasitic reactions within lithium-ion cells are almost always irreversible: there is no effective way to “reform” a lithium-ion cell (retrieve its original properties) in-situ. As a result, for high cycle-life applications there must be almost no undesired side reactions (side reactions should occur less than 0.01 percent as often as the desired reaction). Since side reactions are enhanced at higher temperatures, reaching this target requires clever cooling systems. Heat can dissipate passively in small systems, but larger systems require active thermal management, which adds cost. The optimum design that keeps the cooling costs of a large lithium-ion system within bounds as the system gets larger generally results in a system that also has a lower energy density.

**Sodium-sulfur chemistry** represents a stationary storage system with demonstrated cycle life and calendar life that meets typical grid-scale needs (greater than 5,000 cycles over a 20-year period). Sodium sulfur (NaS) batteries operate at temperatures between 250°C and 300°C. The structure of NaS batteries is inverted compared to the previous cells: the anode and cathode in NaS cells are liquids, and the electrolyte is a solid ionic conductor. The high operating temperature of this cell excludes it from standalone and standby operation, but it also speeds up charging and discharging. The liquid electrode enables these cells to cycle much more quickly, and many more times, relative to the aqueous and lithium-ion cells.

The elements within a NaS cell are abundant (Na, S, Al, O, C), and the heat generation of this system can stabilize operation rather than create parasitic losses. However, the enhanced reactivity of both sodium and sulfur at high temperatures requires precise assembly and power management, which is the cell’s dominating cost, much larger than the raw cost of the materials. To date, the cost of this system has not decreased as its scale has

become larger. NaS batteries have the longest demonstrated use-life of any large terrestrial electrochemical systems (some systems have operated in outer space for even longer), but several recent NaS fires at large grid-connected installations – immune to all known fire suppression methods – have halted further installation of NaS batteries.

## Comparisons

Lead-acid cells are at present the lowest cost and safest of the three. The voltage is restricted by the side reactions of the aqueous electrolyte, especially by the electrolysis side reaction that produces hazardous hydrogen gas (and oxygen gas) from water. The engineering challenge for the lead-acid cell is to extend its life without increasing its cost, for example by finding better ways to reduce the chemical and physical degradation of its electrodes. Even though lead is a toxic metal, the design of a modern battery makes it relatively easy to prevent any environmental exposure. In fact, environmental exposure is almost always the result of gross negligence with respect to end of life removal rather than the result of operational failure.

Lithium-ion cells are the most energy dense of the three systems. The properties of the lithium electrolyte at present limit the per-cycle efficiency and the cycle life of the cell. Manufacturing costs related to materials purity limit widespread implementation at present. The engineering challenge for lithium-ion cells is to maintain per-cycle current efficiency while decreasing manufacturing costs, materials costs, and flammability.

Liquid sodium cells have the longest operating history of the three technologies in grid applications. The abundance and low cost of the active materials is appealing, but the manufacturing and operational tolerances are inherently expensive, due to the reactivity of the materials and temperature of operation. The engineering challenge for sodium-sulfur cells is to decrease cost while increasing safety of operation. Liquid sodium cells should not be confused with sodium-ion cells, which are a new class of aqueous battery.

## The storage frontier

The three chemical systems just discussed are being improved both incrementally and disruptively, but how much these systems will be improved remains to be seen. In parallel, novel battery systems are beginning to be explored that represent larger changes in structure. Bear in mind

that to date, there are only promising beaker-scale experiments on these novel systems, and there is ample reason for caution in extrapolating to grid-scale applications.

To comprehend the current frontier of electrochemical energy storage, it is helpful to appreciate that this frontier actually embraces two diametrically opposed design principles. One strategy accepts significant change as the result of materials transport. The system is designed so that the substantial changes to the chemically reacting surfaces can be reversed by a carefully engineered supporting structure, so that the battery can be cycled a very large number of times. Traditional chemicals are being pursued in this newer geometry; for example, plate metals such as lithium, zinc, and aluminum are being utilized as anodes in this approach. With this strategy, the objective is to utilize every bond in the electrode for energy, so that the resulting system can be compact and light weight. In such systems the structure of the electrodes undergoes a reversible transformation (a “phase change,” analogous to the evaporation and condensation that take a liquid to a gas and back to a liquid). Such phase changes erase all memory of the electrode’s mechanical history and allow a new cycle to start from scratch. The compromise here is that the core electrochemically active system requires substantial supplementary systems to maintain stability, such as pumps and heat exchangers, which add complexity and cost.

A cousin to this first approach, in the sense that it also seeks to maximize the use of the chemical bonds in the structure, is the flow battery (equivalently, flow cell). In a flow battery, the electrochemically active constituents are stored outside the battery and are pumped through it, thereby enabling high capacity.

The second design principle is to minimize the changes induced in the battery when the electrochemically active material is transported from one location in the battery to another. This approach creates “open-framework” systems, where the electrodes contain “atomic tunnels” that allow ions to enter and leave with little to no resultant strain on the electrode structure, resulting in a theoretically unlimited cycle life. The resultant design is a compromise that trades very long cycle life against additional volume (there is much open space that could otherwise be dedicated to energy storage bonds) and weight (in these open framework structure there can be 16 to 24 structural bonds for every single energetic bond).

Among existing batteries, in principle the lead-acid battery can undergo deep discharge cycles, following the first approach, but in practice this battery would last for only a few cycles. Instead, by “underutilizing” the lead-acid system, the lead-acid battery lasts much longer, providing thousands of “shallow” cycles. As for the lithium-ion battery, its chemistry is designed to exploit the second approach, but the first approach is engaged as well, because most lithium-ion variants would suffer from irreversible structural changes if their full capacity were used, and therefore they too must be “underutilized” and restricted to shallow discharge. There are notable exceptions among lithium-ion chemistries that avoid the compromises that force shallow cycles, such as batteries with a lithium-iron-phosphate ( $\text{LiFePO}_4$ ) cathode. But for these cases, another compromise must be dealt with: batteries with these exceptional chemistries can store less electric charge per kilogram than their non-exceptional cousins, such as batteries with a lithium-cobalt-oxide ( $\text{LiCoO}_2$ ) cathode.

What all of these “next generation” approaches have in common is a systematic use of the non-active components in supporting roles. Most modern batteries have a large amount of inactive mass that *could* provide energy but would do so at the cost of cycle life. These new approaches, if successful, will enable much more effective use of the whole structure over thousands of cycles.

## **A hierarchy of demands for storage**

In estimating how quickly batteries will penetrate new markets for grid-scale storage, it is helpful to consider three categories of markets: markets where the needs are dire, moderate, and emergent. In all three categories, costs can be expected to fall as commercialization proceeds.

Dire needs for storage are associated with unpredictable, rare events, such as hurricanes, which create power failures at various scales that lead to damage ranging from severe to catastrophic. These are events where, if people had been able to predict the event, they would have gladly paid for storage at prices far above those at which storage can now be bought. When storage is sufficiently reliable in this domain, the result is “uninterruptible power supply,” and it is bought by customers ranging from data centers to nuclear power plants. In spite of the rarity and unpredictability of catastrophic events, the market for this kind of storage is certain to increase, given

the increased focus on hardening critical loads and enhancing the resiliency of the distribution grid in response to severe weather events. Not only is the cost of storage likely to fall, but the cost of nasty events is likely to increase.

Moderate needs for storage are, essentially, the needs for ancillary services on the grid. These include improvements in frequency and voltage regulation, congestion reduction, and the management of transmission overload. Events triggering these needs are already frequent, and many are not predictable. An increased presence of wind and solar on the grid brings with it greater unpredictability and thus greater demand for solutions that storage may provide in this middle category. Renewables tighten the knot, and storage loosens it.

Emergent needs for storage accompany a world that, contending with climate change, seeks non-carbon electricity and confronts the intermittency of wind and solar energy. This is a world that will prefer to supplement intermittent renewables with multi-hour storage rather than with traditional

natural gas power plants. This class of needs is largely motivated by the arrival of renewable energy.

Dire needs can justify the purchase of high-cost storage when there is reason to believe that the nasty events will occur. The promise is safety for people and vulnerable equipment. Whether moderate needs will be met depends critically on the cost and performance of storage options; demand exists in the marketplace now. The promise is a better performing grid. Emergent needs require storage to be sufficiently low-cost to compete with traditional power generation. The promise is a lower-carbon economy.

An optimistic view would hold that cost reductions will propagate from one market to the next. But are such fundamentally different markets actually related like links in a chain, like stepping stones across a stream? In particular, can the progress that energy storage is making in supplying fast-response ancillary services be translated into the technological advancement required to enable electricity grids that are dominated by intermittent renewables? This is far from certain.