

REVIEW SUMMARY

BATTERIES

Why do batteries fail?

M. R. Palacín* and A. de Guibert

BACKGROUND: We are all familiar with the importance of mobile power sources (automobile batteries, cell phone batteries, etc.) and their seeming tendency to malfunction at just the wrong moment. All batteries show performance losses during their service lives that involve a progressive decrease in capacity (loss of autonomy) and increase in internal resistance, leading to voltage decay and loss of power. Battery aging phenomena evolve at substantially different rates depending on storage or usage conditions (temperature, charge/discharge rates, and voltage operation limits) and are specific to each battery chemistry. The study of the origin of such processes is important for battery calendar-life predictions, but this research is complex to carry out because it involves field trials as well as extrap-

olation from accelerated tests using suitable models.

ADVANCES: Electrification of automotive transportation and renewable energy integration constitute two imperative pathways toward reduction of gas emissions and global warming. These incur challenges in terms of energy storage technologies, for which batteries emerge as a versatile and efficient option. Durability is critical per se in such large-scale applications and also has a direct impact in terms of cost. As a result, efforts toward understanding the mechanisms of battery degradation have intensified in recent years.

Aging and failure mechanisms result from various interrelated processes taking place at diverse time scales, hence their complete

elucidation is a very challenging target. Battery operation upon each charge/discharge cycle should ideally only involve changes in the phases present at both electrodes and modification of their physical properties. However, all battery components can interact with one another to some extent, contributing to a convoluted system of interrelated physicochemical processes in which the influences of temperature and charge/discharge rate are decisive.

Although interactions between the active materials and the electrolyte are largely responsible for aging upon storage, cycling generally

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damages electrode active materials' reversibility because of the mechanical stresses induced by the structural changes taking place. Although both mechanisms are often considered as additive, interactions may occur and some additional factors (such as temperature) have an impact on both. Moreover, the variety of possible parasitic reactions is enhanced by the number of chemical elements present in the cell; this number is lowest for Pb/acid batteries (redox processes involve lead at both electrodes and current collectors are also made of lead) and highest for lithium-ion batteries, which can also comprise a larger variety of subtechnologies depending on the active materials used.

Overall, the current available knowledge on these matters results from a vast combination of experimental and modeling approaches and has greatly benefited from the progressive improvement of available materials science characterization tools.

OUTLOOK: The requirements for battery long-term stability are extremely stringent, and hence the advent of batteries with optimized calendar and cycle life will only be triggered by a full understanding of the ways in which the different systems fail. Thorough studies involving both testing and monitoring of real or model cells under different environments and/or postmortem studies using a wide range of experimental techniques coupled to modeling approaches are crucial to the complete elucidation of aging and failure mechanisms. Such knowledge is vital to developing reliable, realistic operation models, which in turn will synergistically contribute to the development of batteries with optimized calendar life. This is currently a research priority in the field that is expected to yield substantial progress in the years to come. ■



Performance degradation is common to all battery technologies. Failure and gradual performance degradation (aging) are the result of complex interrelated phenomena that depend on battery chemistry, design, environment (temperature), and actual operation conditions (discharge rate, charge protocol, depth of discharge, etc.). Knowledge of such processes is crucial for the widespread deployment of large-scale battery applications such as transportation and the electric grid.

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Why do batteries fail?

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Battery failure and gradual performance degradation (aging) are the result of complex interrelated phenomena that depend on battery chemistry, design, environment, and the actual operation conditions. The current available knowledge on these matters results from a vast combination of experimental and modeling approaches. We explore the state of the art with respect to materials as well as usage (temperature, charge/discharge rate, etc.) for lead-acid, nickel-cadmium, nickel–metal hydride, and lithium-ion chemistries. Battery diagnosis strategies and plausible developments related to large-scale battery applications are also discussed.

Energy storage is a key enabler for modern life. A large spectrum of storage technologies exists today, with wide variation in terms of maturity, amount of energy stored, speed of release (power), efficiency, durability, and cost. Batteries occupy a privileged position in this landscape, as they are highly versatile: Cells can be manufactured in a wide range of sizes that can also be assembled into packs if necessary. Countless technologies could be developed a priori by coupling different pairs of electrodes based on any favored redox reaction. Nonetheless, more than 200 years after Volta's invention, only a few systems have been considered to fulfill all requirements to enable practical development and a mere handful of them are commercially important. Their historical evolution in terms of performance has seen a few disruptive events, such as the patents of the Pb/acid battery in France (Planté, Faure) and Ni-based technologies in Sweden and the United States (Jüngner, Edison) at the turn of the 20th century, and most recently the commercialization of Li-ion technology in Japan (Sony) in 1991.

The versatility of batteries has enabled their use in widely diverse domains of application, from miniaturized devices to large-scale storage plants. The total size of the global battery market accounted for \$54 billion (U.S.) in 2013, with 5% average growth per year between 1990 and 2013. Lithium-ion technology is the most popular at present, with an equivalent to about 38,000 MWh of storage being commercialized in 2013. The proportion used in portable electronics far exceeds that used in alternative or emerging applications such as hybrid and electric vehicles (sometimes known as xEVs). The largest part of the ~1.8 million vehicles sold in 2013 use Ni–metal hydride (Ni/MH) batteries, with Li-ion batteries accounting for roughly

500,000 vehicles (and corresponding to 3500 MWh) (1). Stationary energy storage involves the use of large batteries, and even if it is expected to grow concomitant with renewable energy penetration (2), its present capacity is only 1170 MWh of battery storage, of which ~40% consists of Li-ion batteries. Growth expectations in all sectors are derived from diverse converging forecasts, with an estimated global market by 2020 close to \$32 billion for Li-ion technology alone.

Despite this success, the requirements for long-term battery stability are extremely stringent. As a consequence, a battery's performance is ultimately always modified (degraded) during its lifetime. Users are familiar with this phenomenon even if they are seldom aware of its causes, as they are often specific to each battery technology and are rarely addressed globally. The present paper aims to fill this void.

At first glance, any battery operation may seem extremely straightforward, based on a combination of two redox semi-reactions as taught in high school chemistry class. Yet an intrinsically complex and evolving system exists behind this apparent simplicity. Aside from the requirements for “active” electrode materials and an electrolyte that makes ionic transport possible, practical performance is enabled by alternative “inactive” components such as current collectors (metal foil, grid, foam, etc.), separators (glass fiber or polymeric microporous film in which the electrolyte is embedded), conductive additives (typically metals, inorganic conducting compounds, or different types of carbon), and often some sort of polymeric binder (Fig. 1A). All these contribute to battery function by maintaining the electrode's electronic and mechanical integrity. In addition, batteries are often designed for a particular application, and there is usually a trade-off between the maximum power output possible and the maximum stored energy. Indeed, cells designed for high power output require low internal resistance and low electrode polarization, accomplished by thin electrodes of high surface area. Thus, the inert current collectors, separators, etc., constitute a higher fraction of the mass and volume, and the stored energy density

decreases by comparison to energy-optimized cell designs.

Battery operation upon each charge/discharge cycle brings about a change in the phases present at both electrodes and modification of their physical properties. Ideally, such processes should be fully reversible and should exclusively involve the active materials. However, all battery components can interact with one another to some extent, contributing to a convoluted system of interrelated physicochemical processes, which are dependent on many factors. Some of them are related to practical operation conditions such as charge/discharge rate or temperature.

Basics of battery operation

The chemical energy stored in a battery is the product of capacity and voltage, and is primarily determined by the cell chemistry and electrode materials. Usually, the open-circuit voltage is considered together with the discharge capacity to a certain cutoff voltage. These are not absolute, independent measures; they are heavily affected by electrode kinetics, and thus they depend on discharge rate and temperature (3). The fundamentals of the most commercially relevant rechargeable battery systems (4) are given in Table 1.

The maximum electric energy that can be delivered by the electrode active materials depends on the change in free energy ΔG of the chemical reaction involved (Table 1). Upon operation, irreversible energy losses occur because batteries exhibit an intrinsic internal resistance (R): Joule heating (I^2R) and ohmic drop (IR drop). These losses are all related to the current flowing through the cell (I , the charge/discharge rate), which is usually expressed in terms of C/n rate, where n is the time (in hours) to achieve the cell capacity (C). As the current drain of the battery is increased, losses increase and the amount of energy recovered is reduced. In contrast, at extremely low current drains, energy can approach theoretical expected values. This explains, for instance, why a primary battery used to its end-of-life (EoL) in a high-drain application (e.g., camera flash) can subsequently be used to power a quartz clock, requiring much lower current.

The operation of Pb/acid cells involves major structural reorganization of the electrode active materials, with dissolution and reprecipitation of lead sulfate or lead dioxide at each cycle. In the case of Ni-based batteries, the Cd electrode also involves a dissolution-precipitation mechanism, whereas the reaction at the MH electrode takes place in the solid state. For the Ni(OH)₂ positive electrode active material, a solid-state redox reaction involves reversible de-insertion of H⁺ from the layered crystal structure with concomitant modification of its stacking sequence (5). Lithium-ion batteries operate through reversible (usually topotactic) insertion of Li ions in the structure of both electrode materials; the most common materials are graphite for the negative electrode and layered transition metal oxides or lithium iron phosphate for the positive electrode (Table 1). Materials operating through alternative redox mechanisms enabling higher

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energy densities have been intensively investigated (6) but have not yet reached the commercial stage.

The electrolyte is ideally a chemically inert medium that simply impregnates both electrodes and the separator to enable ionic transport. Aqueous electrolytes (either acid or alkaline) are used in “traditional” battery technologies such as Pb/acid, Ni/Cd, and Ni/MH. These are, however, unstable at the operation potentials of Li-ion batteries, and a mixture of organic solvents (commonly alkylcarbonates) is used, typically with 1 M LiPF₆ dissolved. This adds some complexity to the picture, because the electrochemistry in these media is much less developed. The energy separation of the lowest unoccupied molecular orbital and the highest occupied molecular orbital of the electrolyte (LUMO and HOMO, respectively; Fig. 1B) determines the thermodynamic cell’s electrochemical stability window.

The electrolyte is crucial in generating stable electrode/electrolyte interfaces and thus plays a key role in cycle life (defined as the number of

charge/discharge cycles that a battery can sustain while keeping a given percentage of its initial capacity, usually 80%, set as EoL). For the case of Li-ion technology, electrolyte solvents are unstable below ~0.8 V versus Li⁺/Li and above ~4.5 V versus Li⁺/Li in the presence of the electrode materials, which are strongly reducing/oxidizing. Consequently, electrolyte solvent degradation reactions take place at the electrode/electrolyte interfaces, which often also involve the electrolyte salt and water impurity traces. The resulting insoluble products form a solid protective passivation layer adhering to the surface of the negative electrode (termed the solid-electrolyte interphase, or SEI) (7–9). An interphase is also formed at the surface of the positive electrode, sometimes called the surface layer (SL) to distinguish it from the one formed at the negative electrode. Thus, cell operation is made possible through proper passivation of both electrode surfaces, which enables successful operation of the electrolytes outside their thermodynamic stability windows (10). However, overcharge (supply of charge in excess of that

required by electrode materials) will still lead to side reactions, such as irreversible electrolyte decomposition (11) with gas generation.

In aqueous technologies, the operating voltage is limited by water decomposition; the Pb/acid battery voltage is higher than that of Ni-based technologies, owing to a much higher hydrogen overvoltage. Overcharging leads to water electrolysis with formation of oxygen at the positive electrode that can diffuse to the negative electrode and recombine by reduction at its surface. Thus, effective battery designs enabling rapid transport of oxygen and recombination efficiencies close to 100% provide overcharge protection and enhanced safety (12, 13).

Battery degradation and failure

Although battery operation should ideally entail the reversible redox reactions mentioned above, involving exclusively electrode active materials (or some electrolyte components for Pb/acid and Ni/Cd; Table 1), the real situation is much more complex, and additional physicochemical processes

Fig. 1. Schematics of typical battery cell and example of energy levels involved. (A) Architecture of a cell with composite electrodes. (B) Illustration of the energy levels involved in a Li-ion electrochemical cell. The dashed red, blue, and green lines correspond to the chemical potential of Li in the negative electrode, the chemical potential of Li in the positive electrode, and a typical placement for the voltage window of the electrolyte, respectively. V_{oc} , open-circuit voltage of the cell; μ , chemical potential. [(B) adapted with permission from (57)]

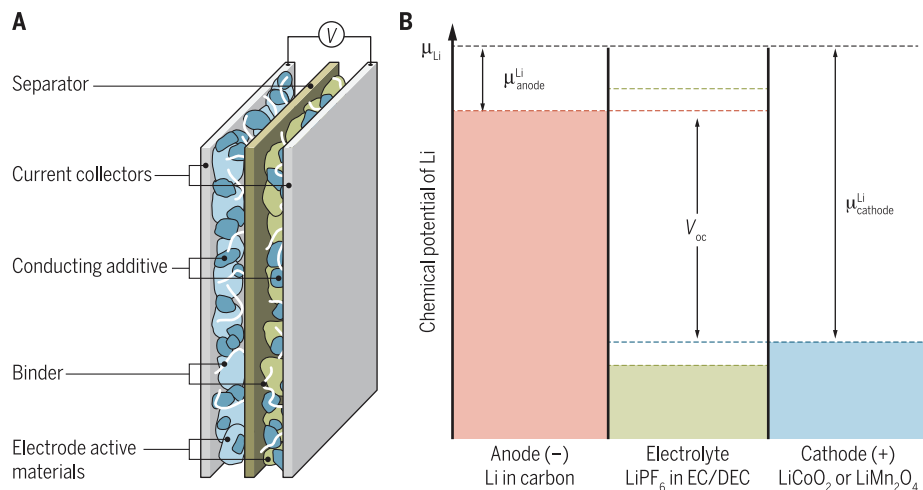


Table 1. Chemical reactions and performance figures of merit for commercially relevant rechargeable battery technologies.

Technology	Electrolyte	Overall reaction	Cell voltage (V)	Specific energy (Wh/kg)	Operating temperature (°C)
Pb/acid	Sulfuric acid (aq.)*	$\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$	2.04	30	-25 to +50
Ni/Cd	Alkali hydroxide (aq.)†	$2\text{NiOOH} + \text{Cd} + 2\text{H}_2\text{O} \rightarrow 2\text{Ni(OH)}_2 + \text{Cd(OH)}_2$	1.3	50	-40 to +60
Ni/MH‡	Alkali hydroxide (aq.)†	$\text{NiOOH} + \text{MH}_x \rightarrow \text{Ni(OH)}_2 + \text{MH}_{1-x}$	1.35	65	-20 to +60
Li ion	LiPF ₆ (organic solvents)	$\text{Li}_{1-x}\text{MO}_2 + \text{Li}_x\text{C}_6 \rightarrow \text{LiMO}_2 + 6\text{C}$	3.6§	150 to 270	-30 to +60¶
Li polymer#	Li salt** (polyethyleneoxide)	$x\text{Li} + \text{V}_2\text{O}_5 \rightarrow \text{Li}_x\text{V}_2\text{O}_5^{\dagger\dagger}$	3	140	60 to 100

*The electrolyte (sulfuric acid, $d = 1.27 \text{ g/cm}^3$) and electrolyte solvent (water) participate in the reaction, being consumed during discharge and regenerated upon charge.

†Typically a mixture of KOH, NaOH, and LiOH with overall concentration 4.5 to 8 M. NaOH and LiOH are added to improve chargeability through increase of the oxygen release overpotential. ‡The anode is an alloy, most frequently AB₅, where A is a rare earth (mostly mischmetal to limit cost) and B is Ni, Co, Mn, and/or Al. §With graphite (C) anode and layered transition metal oxide cathode such as LiCoO₂ (LCO), LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ (NCA), LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ (NMC 1/1/1), or other compositions containing Ni, Mn, and Co, which exhibit more stable crystal structures upon lithium de-insertion and thus larger capacity. Alternative cathodes such as LiMn₂O₄ (LMO) or LiFePO₄ (LFP) yield cell potentials of 3.6 V and 3.2 V, respectively, and somewhat (15%) reduced energy densities due to lower specific capacity and lower voltage, respectively.

¶The lower figure corresponds to industrial long-life batteries; the higher figure applies to low-power, limited-life batteries for portable applications. ¶¶Can reach somewhat expanded low or high limits in particular applications with specifically designed batteries. #Not to be confused with Li-ion chemistry with liquid electrolyte embedded in a polymer, sometimes commercially (and misleadingly) denoted “polymer Li-ion.” **Commonly LiN(CF₃SO₂)₂ (usually denoted LiTFSI). ††More recently, LiFePO₄ has also been introduced as positive electrode material without major change in performance.

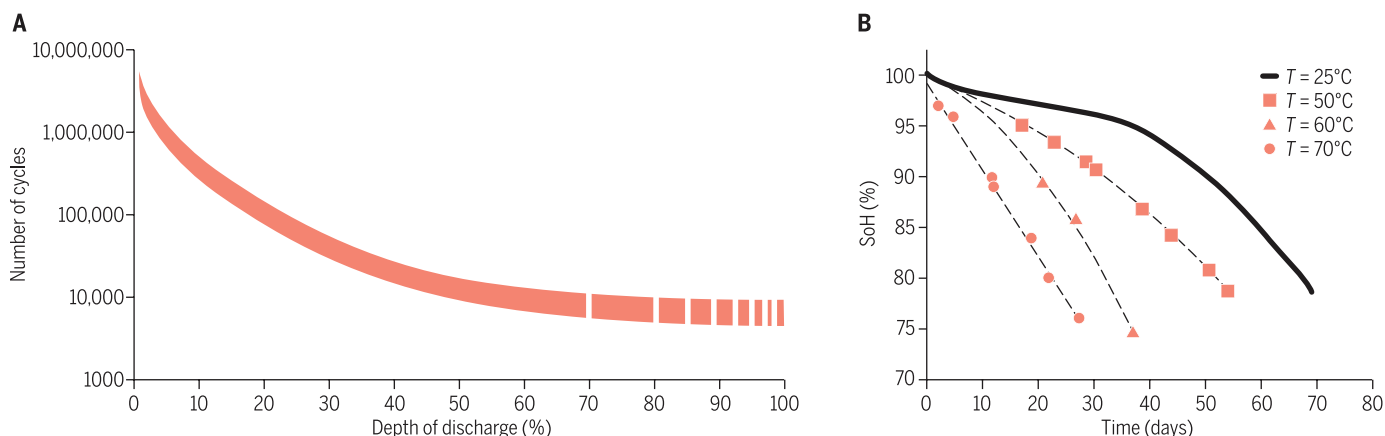


Fig. 2. Influence of depth of discharge and temperature on battery performance degradation. (A) Cycle life as a function of DoD for Li-ion cells operating at 25°C. (B) State of health (SoH, defined as the discharge capacity of an aged cell relative to the discharge capacity of the same cell when it was new) as a function of time for Li-ion cells cycling at a rate of 1C at different temperatures. [Adapted with permission from (17)]

occur that may involve any battery component. These are obviously dependent on battery chemistry, with the number of possible parasitic reactions being enhanced by the number of chemical elements active or present in the cell. This number is lowest for Pb/acid batteries (redox processes involve lead at both electrodes, and current collectors are also made of lead) and highest for Li-ion batteries, which can also comprise a larger variety of subtechnologies depending on the active materials used (Table 1). The type and extent of such reactions is also affected by the environment (temperature) and conditions of use [discharge rate, charge protocol, depth of discharge (DoD), etc.] throughout the battery lifetime. For example, batteries used in uninterrupted power supply (UPS) units remain in float condition (compensating any self-discharge of the battery by constant charge at very low current) and are normally subjected to a limited number of cycles during their life, whereas pure hybrid electric vehicles usually operate at low DoD but in a partial state of charge, and batteries in fully electric vehicles or portable electronics function at high DoD (or charge-depleting mode).

The above-mentioned side reactions can cause phenomena leading to sudden failure (cell drying, short circuit, thermal runaway) or can manifest indirectly via a large variety of symptoms that contribute to battery “aging” with progressive performance degradation to EoL (14). Sudden failure is often encountered in Pb/acid 12-V SLI (starting, lighting, and ignition) six-cell batteries used to start vehicle internal combustion engines. This may happen on cold winter mornings, as when an aged battery with decreased power and enhanced-viscosity electrolyte is unable to start an engine that uses a higher-viscosity motor oil. Yet it can also take place in hot climates, as when temperature-enhanced corrosion causes grid short circuits or disconnection. The study of the origin of such processes is important for battery calendar-life predictions, but such research necessarily involves either field trials or extrapolations from accelerated tests using suitable models (15). Moreover, Li-ion battery

designs are not always optimized to provide the longest possible calendar life. Although this is the case for large batteries used in industrial applications, smaller ones used in portable electronics are merely targeted to outlive the devices they power (~3 years for cell phones), and their designs are optimized for specific energy (autonomy).

The main generic manifestations of battery aging are observed both during use and upon storage: a progressive decrease in capacity (loss of autonomy) and an increase in internal resistance leading to voltage decay and loss of power. Cycling generally damages electrode active materials’ reversibility, especially at high DoD (1000 cycles at 100% DoD is a heavier duty than 10,000 cycles at 10% DoD) (Fig. 2A). This can be rationalized in terms of the mechanical stresses induced by the changes taking place at the electrode active materials as a function of state of charge (e.g., intercalation of lithium ions in a graphite electrode leads to 12% expansion of graphite along the *c* axis for a fully charged electrode). In contrast, interactions between the active materials and the electrolyte are mostly responsible for aging upon storage for Li-ion or MH electrodes. Although both mechanisms are often considered as additive, interactions may definitely occur and some additional factors (e.g., temperature) can have a substantial impact, which adds even more complexity to the scenario.

Fast operation rates involve higher losses in terms of polarization and Joule heating (and hence a temperature increase). The general trend is an increase of degradation with temperature (Fig. 2B), the cause being mostly the enhanced rate of side reactions involving electrode/electrolyte interfaces, which take place both upon cycling and upon storage. This is nicely exemplified by the results of a study dealing with SLI Pb/acid batteries sampled from 24 U.S. cities showing a strong correlation between battery service life and the number of days per year with maximum temperature above 32°C (90°F) (16). The usual way of scientifically analyzing

the influence of temperature is to assume that side reaction rates follow an Arrhenius law (i.e., they increase exponentially with *T* through a coefficient linked to an activation energy). Yet this is no easy task, as several reactions may simultaneously or successively take place, each with its own activation energy and rate constant (17).

Performance degradation through battery lifetime is common to all battery technologies and can evolve at different rates, depending on operation conditions (temperature, charge/discharge rate, and voltage operation limits). Still, aging processes are ultimately rooted in chemical reactions between battery components and are thus technology-specific. These reactions are complex and in some cases not fully elucidated. Below, we outline the currently assessed trends for the three main rechargeable battery technologies, focusing on main reactions while emphasizing aspects related to cell design or electrode technology.

Pb/acid batteries

Pb/acid batteries still constitute the largest part of the worldwide battery market share in terms of MWh (7). Aside from SLI batteries (60 million produced each year), they are also used in small traction vehicles used in airports, golf courses, industry (forklifts), motorized wheelchairs, and stationary applications to cover power backup in hospitals or emergency services and alarms, among others.

Some of the failure mechanisms for SLI batteries—by far the most common type of Pb/acid battery in use today—are simply the result of mechanical shocks (broken or damaged containers or terminals including electrolyte leakage); others depend on use (e.g., electrolyte dryout due to overcharge) and choice of design (18, 19). Positive electrode grid corrosion or fracture and loss of contact have been observed, which can be mitigated by improving corrosion resilience with the use of Pb-Ca or Pb-Ca-Sn alloys (for the negative and positive electrodes, respectively) and through control of grid microstructure to avoid grain growth in the casting process. It is also noteworthy that antimony-containing alloys

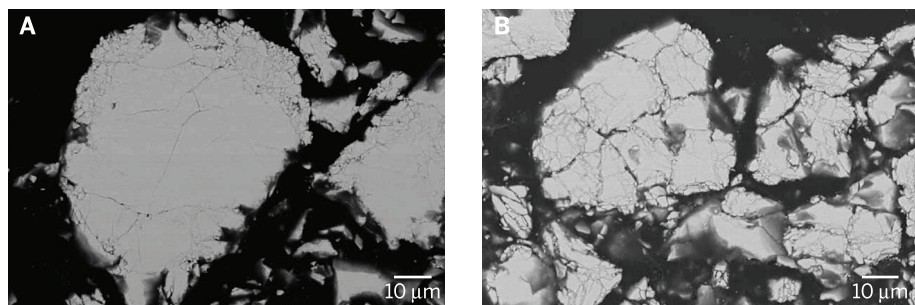


Fig. 3. Scanning electron micrographs of electrode cross sections. (A) Before cycling; (B) after 100 cycles. These images (magnification 1000 \times) show that the active material surface exposed to electrolyte is much larger on cycled cells, which in turn enhances the corrosion rate.

used in the positive electrode grids for easier castability result in corrosion and further migration of antimony ions to the negative electrode, which decreases the hydrogen overvoltage and hence results in decreased chargeability.

Loss of active material adhesion can also take place, which may lead to short-circuit after sedimentation (mud formation) unless pocket plate separators wrapping one electrode are used. The growth of large crystals of insulating lead sulfate on the negative electrode, concomitant with the decrease in sulfate concentration in the electrolyte, has also been assessed (termed “sulfation”) (20). Such crystals exhibit very slow reaction kinetics that may not enable operation. This issue can be alleviated by addition of higher amounts of carbon to the electrode to enhance electronic conductivity, but still restricts the application of Pb/acid batteries in hybrid electric vehicles (HEVs) (21).

In addition, large industrial Pb/acid batteries used in UPS or stationary applications may suffer from electrolyte stratification (development of a vertical sulfuric acid concentration gradient) (22), which can result in nonuniform usage of the active material and is mitigated by setting the battery to deliberate gassing during extended overcharge. Finally, because recombination efficiency never reaches 100%, there is a progressive loss of water and dryout of the electrolyte, which enhances recombination current and in turn heat emission, which can ultimately result in thermal runaway for valve-regulated aged batteries.

Nickel-based batteries

There are two main Ni-based battery technologies widely used in different applications: Ni/Cd and Ni/MH. Globally, Ni/Cd sales decreased by 6% per year between 2002 and 2012 while Ni/MH increased by 5% per year in the same period. Both types of battery are fabricated as small sealed cylindrical cells for portable applications and as large prismatic cells or modules for industrial applications. Although small Ni/Cd cells are no longer in use for portable devices because of the toxicity of cadmium and the difficulty of collecting them for recycling, they are still used for emergency lightning units (ELUs) as they can withstand 4 years floating at 40° to 55°C better than other chemistries. Industrial Ni/Cd batteries,

either flooded (with excess electrolyte) or needing low maintenance (occasional addition of water to compensate for electrolyte consumption), are renowned for their very long life—up to 20 years—and reliability in either cycling or standby applications. This is related to the very reversible electrochemical reactions, excellent stability of the active materials, and very small number of side reactions (which allows extremely low fading even at 100% DoD) and to the existence of commercial batteries with robust design that can withstand mechanical abuse. Small Ni/MH batteries are used in home appliances (cordless phones, toys) and are starting to be used for ELUs, whereas larger cells are used in hybrid vehicles such as trams, buses, and cars (such as the Toyota Prius), where their absence of maintenance is a key advantage compensating for their higher cost.

The operation in concentrated alkaline electrolyte in oxidizing medium (presence of oxygen when the cell is charged) leads to decomposition of organic polymers present in the cell (separator, fibers, binder) and formation of carbonates in electrolyte, which decreases its ionic conductivity and hence the performance. Moreover, alkali carbonates have a limited solubility and can precipitate, which would enhance this effect.

Degradation phenomena at the positive Ni electrode are largely dependent on the electrode technology. Indeed, the insulating character of Ni(OH)₂ (usually also alleviated by partial nickel substitution for cobalt and zinc) results in conducting additives being essential. Sintered plates are made of sintered nickel particle substrates on which the active nickel hydroxide material is deposited by chemical precipitation or by electrochemical reduction of nickel nitrate solutions. These are thus very conducting, as the active material is always in contact with the metallic substrate that also acts as current collector. Nonetheless, such electrodes are more expensive to manufacture, and they sacrifice capacity on a weight and volume basis. Alternatively, electrodes pasted on a metal foam, mesh, or sheet require the use of a plastic binder and conducting cobalt oxide and hydroxide additives, commonly added by simple mixture with the nickel hydroxide active material particles or coating their surfaces. Yet such cobalt-containing phases do chemically evolve and are irreversibly reduced

upon battery operation, which brings about a decrease in the electrode conductivity.

With respect to the cadmium negative electrode, crystal growth can be promoted at the expense of nucleation under certain cycling and storage conditions, which results in a reduced active electrochemical surface and lower efficiency. In contrast, a pulsed charging mode is associated with long rest periods that can result in the growth of cadmium particles (metallization), which may cross the separator and induce soft shorts (nonviolent short circuits perceived by the user as high self-discharge).

Degradation of the negative electrode in the Ni/MH technology takes place mainly through two related processes (23–25). These involve corrosion of the alloy active material through surface reaction with the alkaline electrolyte and further pulverization due to stresses induced in the structure by hydrogen absorption/desorption upon cycling (Fig. 3). Fracture exposes new fresh electrode surfaces and corrosion proceeds, consuming water from the electrolyte, which results in cell dryout and enhanced resistance. Therefore, Ni/MH batteries under normal use conditions exhibit the same progressive aging linked to the positive electrode, and additionally a gradual increase of the internal resistance related to corrosion of the negative electrode. Such corrosion processes can lead to insoluble (mostly metal hydroxides) or soluble products, which can then interact with the positive electrode. For instance, incorporation of aluminum into the crystal Ni(OH)₂ lattice results in an increase of the nickel oxidation potential and hence reduced charge acceptance. Aluminum content in the positive material is commonly taken as a measure to assess the corrosion level of the negative material (26).

Nickel-based batteries suffer from what is commonly termed “memory effect,” which manifests in discharge taking place at a lower potential or, if a cutoff potential for discharge is set, as a loss of discharge capacity (27). This effect results from the combination of different phenomena that are dependent on electrode technology and battery operation conditions, all entailing the modification of phase composition at the electrodes causing operation at lower potential. One phenomenon is cadmium alloying with a nickel-containing electrode substrate (sinter or foam) to form the Ni₅Cd₂₁ alloy, which is reduced at lower potential than Cd. Alternatively, the phase present in the positive electrode in the charged state (β -NiOOH, which exhibits a layered structure) can, upon overcharge in concentrated electrolyte, be transformed to the γ polymorph, which exhibits a higher nickel oxidation state and co-intercalated alkaline ions and water molecules from the electrolyte in the interlayer space. The reduction of this phase takes place at 70 to 100 mV lower potential than that of the β phase. Finally, in electrolytes containing Li⁺ ions (Table 1), exchange with protons in the positive electrode active material can take place with formation of LiNiO₂ (isostructural to β -NiOOH). Again the effect is reduction at lower

potential, which is magnified at high currents because of a difference in reaction kinetics. Finally, β -NiOOH is metastable, and proton rearrangements in the crystal structure upon prolonged storage can result in reduced electronic conductivity, which enhances ohmic polarization. Because the above-mentioned reactions are mostly reversible, the memory effect can be suppressed through a full discharge to low potential to promote full reduction of all involved phases prior to complete recharge.

Li-ion batteries

Li-ion batteries have now been in commercial production for 25 years. Their development, in parallel with the growth of the consumer electronics market, is a striking example of synergy—an application-driven product with constant research-driven improvements in performance. This has enabled diversification of the technology into several subfamilies tailored to meet application needs. The ever-increasing energy density has sometimes been outpaced by practical requirements, as for cell phones requiring continuous operation/connection and large display screens. Transport (xEV) applications are especially challenging because the energy density determines the vehicle autonomy range but safety constraints force some compromises that affect the choice of specific electrode materials, cell designs, and battery management. Lifetime performance is crucial, and U.S. Advanced Battery Council (USABC) goals involve the extension of battery life to 15 years. In this context, identification of the causes of battery degradation is critical, and research efforts in this direction have recently intensified.

Li-ion batteries under normal use conditions do exhibit progressive aging, namely gradual decrease in discharge capacity caused by growth of internal resistance, which manifests as a loss of autonomy for the powered device. Such phenomena (28–30) arise from the combination of some general mechanisms with reactions specific to the particular electrode materials used in each Li-ion battery chemistry. Although the choice is more limited on the negative electrode, enlisting almost exclusively graphite, the positive side involves a larger spectrum of compounds (Table 1).

Capacity decrease for positive electrodes is parallel to enhancement of internal resistance, except for LiFePO_4 , which exhibits lower operation voltage. This can be due to different interrelated phenomena such as decreased ionic conductivity or modification of surface properties as well as reactivity with the electrolyte. Overcharging the positive electrodes, especially those operating at higher voltage, can lead to gas release from electrolyte oxidation as well as oxygen loss from the crystal structure of layered LiMO_2 oxides. This causes both degradation of the active material and an increase in cell internal pressure. In addition, as a result of the absence of recombination mechanisms, the reaction of emitted oxygen with the electrolyte represents a safety concern. The rate of solvent

oxidation is related to the operating voltage but depends as well on the composition and surface area of the active material. Furthermore, it is also largely affected by the surface area of the carbon additives commonly used to enhance electronic conductivity in the electrode. Finally, some positive electrode active materials may also suffer from partial dissolution. This can be related to specific operation conditions (i.e., high temperature) or reactivity with HF (31), which is formed by LiPF_6 hydrolysis with trace water impurities and can be temporarily present in the cell prior to its reaction to form LiF and hydrogen at the negative electrode upon charge. Metal ions (Fe^{3+} , Mn^{2+} , Co^{3+}) present in the electrolyte can be reduced in contact with the negative electrode, damaging the SEI, and can further catalyze electrolyte decomposition.

The two major factors contributing to loss of negative electrode performance are SEI instability and lithium metal plating. Lithium deposition may occur at high charge rates (and thus high polarization, enabling the Li metal deposition potential to be reached) or low operation temperatures (16, 32). At low temperature ($<10^\circ\text{C}$), the diffusion of Li^+ ions inside the graphite structure becomes slow, and Li metal deposition on the surface of the negative electrode can take place with risk of dendrite formation and short circuit. In addition, deposited Li reacts to form its own SEI, consuming electrolyte and lowering the interface porosity, thereby creating inhomogeneities in the electrode. As a result, the cell exhibits both decreased power (due to slower kinetics) and lower capacity (due to loss of active lithium ions in the cell).

An optimal SEI (ionically conducting, electronically insulating, and mechanically resilient) that is stable both upon cycling and storage is critical to long calendar life (33–35). Typical SEI degradation pathways are partial dissolution at high temperature or crack formation due to mechanical stresses inherent to electrode operation. These result in exposure of fresh naked graphite surfaces to the electrolyte on which an additional SEI grows, consuming electrolyte and enhancing electrode resistivity. The thermal breakdown of the SEI commonly starts around 110°C , well below exothermic positive electrode degradation reactions that take place above 200°C and can ultimately yield to thermal runaway (36, 37). SEI properties are extremely composition-dependent and are thus determined by the electrolyte used. This explains why most commercial battery electrolyte formulations are complex and commonly enlist some film formation additives (such as vinylene carbonate) (38). The SEI is formed in the first battery operation cycles (commonly called formation cycles) that are the final step of the manufacturing process, and is usually accompanied by the release of gaseous decomposition products. These cycles are usually performed under specific temperature and cycling rate conditions to minimize the electrochemical capacity involved and commonly result in irreversible consumption of $\sim 15\%$ of the active lithium ions initially present in the cell. Thus, they

have a substantial impact on cell capacity balancing (i.e., optimization of the ratio between the mass loadings of the two electrodes) for optimal use of active materials and hence affect the maximum achievable cell energy density. In an ideal scenario, this capacity balance would not change over the cell life, but this is seldom strictly the case, as it is modified by most of the aging processes mentioned above (Fig. 4) (39–41). Aside from lower energy density, unbalanced cells can exhibit safety hazards due to “overcharge” of the limiting electrode, which in the case of the negative electrode will typically result in lithium metal deposition. To address this contingency, cells are in practice built with an excess of negative active material. This is a compromise strategy to enhance safety at the expense of cell energy density.

Battery monitoring and diagnosis

The users' requirement of permanent knowledge of the remaining battery autonomy (or state of charge, SoC) and state of health (SoH, a term applied to diverse battery indicators, with 100% corresponding to the battery ideal condition in absence of degradation) can only be fulfilled through adequate battery diagnosis protocols based on the identification and monitoring of critical parameters.

The simplest diagnostic system (the “magic eye”) can be found for the Pb/acid technology, in which the electrolyte density varies between the fully charged and discharged states (typically from $\sim 1.27\text{ g/cm}^3$ to $<1.1\text{ g/cm}^3$ in SLI batteries). It consists of three colored (green, orange, and black) small balls with different densities that are immersed in the electrolyte. Battery status is inferred through a window in the battery cover by the color of the floating ball, which is determined by the electrolyte density and thus SoC. In this case, diagnosis is achieved by human intervention, is limited to three predefined levels, and does not involve any data storage. Li-ion batteries lie at the other extreme in complexity of monitoring and diagnosis protocols. For cells using layered cathodes, the discharge curve at different temperatures is precisely known and the SoC is extrapolated from the cell voltage measured in rest periods or discharges at low current. However, more sophisticated procedures are required for LiFePO_4 , as it exhibits a flat voltage discharge curve. In all cases, sensors are typically implemented at the cell level to monitor voltage, current, and temperature. Data acquired are transferred, stored, and analyzed through a battery management system (BMS). These systems started to be developed at the beginning of the 1990s by Texas Instruments, Ericsson, and Motorola and consist of electronic cards with specifically designed diagnosis and active control algorithms based on battery operation models (42). The fabrication quality of the cells or packs, and the knowledge of their behavior in every application environment, is crucial for building reliable models that can be successfully implemented in BMSs to manage battery operation. Such models rely

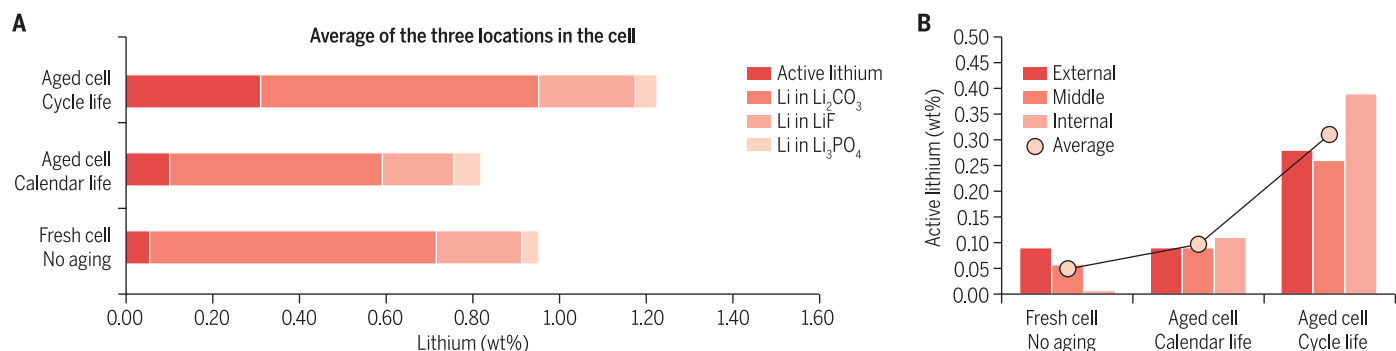


Fig. 4. Evolution of active lithium upon aging of a Li-ion cell. (A) Results of chemical analyses to determine active lithium in the negative electrodes of fresh and aged commercial Li-ion cells. Calendar life denotes 1.5 years of storage at 60°C and 60% state of charge; cycle life denotes 4200 hours of operation at 20°C with 10% DoD. Values for samples taken from the external, middle, and internal parts of the cell are given. (B) Relative quantification based on the lithium compounds actually present in the electrode. [Reprinted with permission from (39)]

on results of testing under different working conditions (temperature, discharge rate, DoD, charge protocol, etc.) and analysis of incremental capacity (43, 44) or differential voltage (45–47), and their use is compulsory to guarantee battery safety and ensure as long a cycle life as possible.

High-precision coulometry and calorimetry have recently proved to be very effective to detect side reactions contributing to performance degradation (48, 49). Yet battery aging and failure mechanisms result from various interrelated processes at diverse time scales, so their complete elucidation and understanding remains a complex and challenging target. Although researchers will take advantage of the benefits in situ and in operando techniques (50), the practical relevance of the outcome needs to be assessed as the test cells are designed to meet analytical requirements (in terms of geometry, size, etc.) and may not be representative of real batteries. Testing of aged electrodes in newly assembled cells (51) coupled to postmortem studies to probe any battery component sampled from distributed cell/electrode locations can provide critical information, especially if a wide spectrum of complementary experimental techniques is used (elemental analysis, optical and electron microscopy, diffraction, nuclear magnetic resonance, infrared, Raman, x-ray photoelectron spectroscopy, etc.) (52–56).

Overall, a smart combination of all such approaches is essential to elucidate the reaction mechanisms accounting for the observed loss in performance upon operation. This knowledge is crucial to developing reliable realistic operation models, which in turn will synergistically contribute to the development of batteries with optimized calendar life.

Conclusion

Although the growth in our understanding of the structure-property relationships of electrode materials has enabled steady progress in battery performance, especially in the case of Li-ion technology, the study of aging and failure mechanisms has developed at a much slower pace. This is mostly due to their intrinsic complexity,

as batteries are multicomponent chemical reactors that can differently evolve through their lifetime depending on their specific design, environment, and operation conditions.

Research efforts in this direction have recently intensified as a result of two different factors: (i) the progressive improvement of available experimental and modeling characterization tools coupled to the fundamental knowledge gained through materials research, and (ii) the need and opportunity for batteries to embrace larger-scale energy storage, for which durability is critical per se and also has a direct impact in application costs. Aside from progress in materials performance and tailored cell design, improvements in the understanding of the mechanisms underpinning battery degradation are required for enhanced xEV market penetration and for the widespread deployment of stationary electrical energy storage to enable a more efficient grid in the years to come.

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