LEAD-ACID BATTERIES ARE NOT GOING AWAY
A Technical Comparison of Lead-Acid and Lithium-ion Batteries

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Introduction

With the introduction of lithium-ion technology into the market by Sony in the early 1990’s, lithium- ion (Li-ion) technology is increasingly being looked at as a most desirable energy storage technology for small and midsize standby power and energy storage applications. The progress with lithium was initially driven by consumer electronics and has now dramatically changed the market with respect to “mobile” batteries like NiCd or NiMH. Based on the primary positive characteristics of Li-ion technology that provide high energy content and good cycle performance, along with the progress of material and production technologies, lithium-ion batteries have been successfully introduced into the market for Battery Electric Vehicle (BEV) or Plug-in Hybrid Electric Vehicle (PHEV) applications.

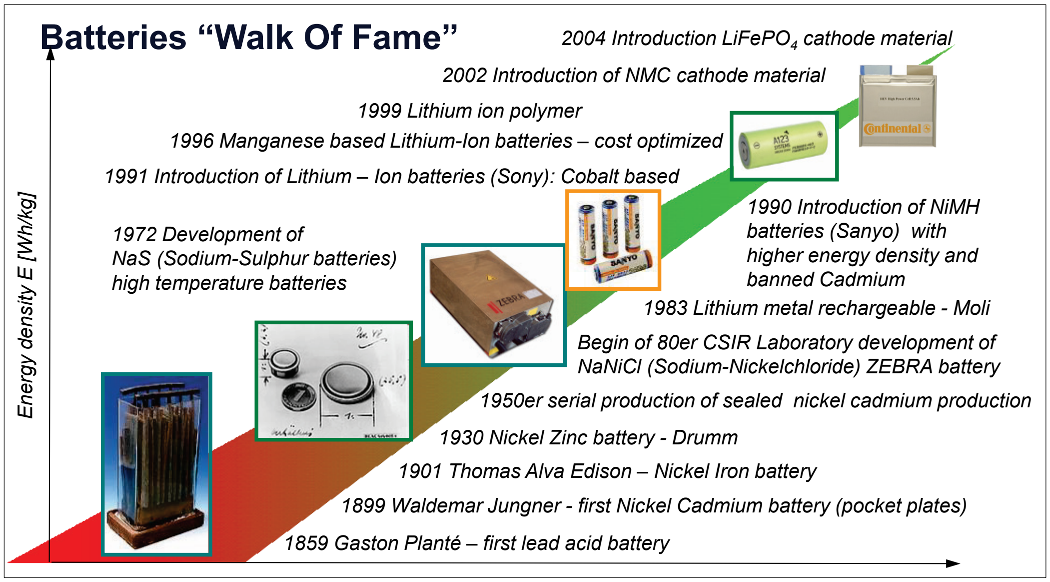


Figure 1. Influence of SOC on the operational life time of lithium-ion cells (NMC cathode)

If we look at the evolution of battery technology as shown in Figure 1 above, we see that lithium is a rather young technology in relationship to lead-acid batteries, with less than 25 years of actual field experience. Continued improvement of the characteristics of lithium-ion is forecasted, and during the next several years that development potential will accelerate. The success of lithium batteries for consumer and electro-mobile applications confirms that lithium-ion technology is fully accepted for these applications. Now lithium-ion technology is looking for new applications, mainly driven by the high investments made in the production of large format cells (> 20 Ah) and the delayed growth of the electric vehicle (EV) market in comparison to the original forecasts. Lithium-ion battery manufacturers are now focused on replacing legacy lead-acid batteries in applications where lead-acid batteries have traditionally dominated[1]. The question is, will lithium-ion technology dramatically change the industrial stationary market as we know it, or will the lead-acid battery remain attractive?

Standby Applications

If we look at the primary characteristics of the lithium-ion technology, on the surface it appears that the technology can be a serious alternative for stationary standby battery markets, especially in the traditional stationary battery applications that provide standby backup power in substations, power generation plants, UPS data centers and telecommunications. This begs the question: are the primary characteristics of lithium-ion technology really essential or required for standby battery operation?

The major electric utilities, especially the investor owned utilities or utilities connected to the Bulk Electric System (BES) in North America which are governed by certain NERC mandates, have typically used vented-lead-acid (VLA) standby batteries for protection and control switchgear, emergency lighting, SCADA and other related applications. They use both VLA and the valve-regulated-lead-acid (VRLA) batteries for their office administration (UPS) and private telecommunications networks.

In a UPS application the battery is delivering anywhere from 5-1000 kWB of power at a battery voltage of 380 - 550 V with a typical discharge/bridging time of 5-30 min. The applied capacity of the battery can be anywhere from 7 to greater than 1500 Ah depending on specification requirements. Larger capacities are realized very often by paralleling several single strings of batteries. Today, the battery utilized more often than not is a VRLA, 12V monobloc battery. Organizations with a high reliability, mission critical requirement often still use the VLA cell. This operation is typically a float operation with equalizing charges given periodically. There are usually very few deep discharges that occur but there can be frequent small discharges. In most cases the loads on the battery are high in relation to the nominal capacity.

For the longest time the Central Office was the switching center for transporting all voice communication and VLA's were the battery of choice. With the advent of mobile communications and the digitizing of voice, video and data, the telecommunications industry utilizes a combination of battery types that include both the VLA and the VRLA cells (individual 2V cells and 12V monoblocs), and in some instances even Ni-Cd's.

The important common factor in all of the applications described above is that these are always maintained and operated at 100% state-of-charge (SOC). That being the case, let us now look at the typical aging of lithium-ion cells as driven by SOC in operation and compare that with the lead-acid cell. Understand that this paper will not focus on every type among the various characteristic subsets but will highlight main characteristics.

Depending on the lithium-ion chemistry, the SOC can dramatically influence the aging speed of the battery (Figure 2). Typically, when the battery is kept at a full state of charge the aging of the lithium battery is mainly driven by the development and growth of the SEI (solid electrolyte interface) at the negative plate (Figure 3). Other aging criteria are: degradation of crystalline structure of positive material (Cathode), graphite exfoliation, metallic lithium plating (during charging process), build-up of passivation film, limiting of active surface area and clogging of electrode small pores.

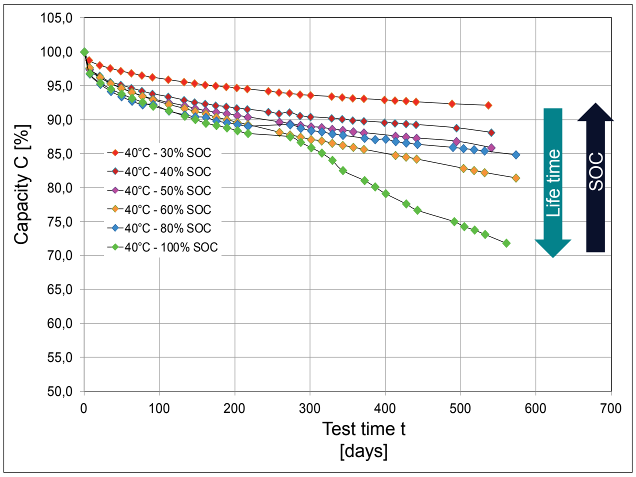
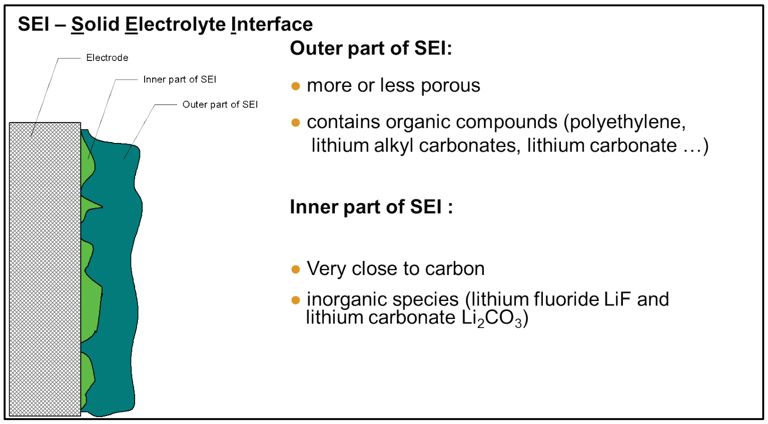


Figure 2. Influence of SOC on the operational life time of lithium-ion cells (NMC cathode)



SEI – Solid Electrolyte Interface

Outer part of SEI:

- more or less porous
- contains organic compounds (polyethylene, lithium alkyl carbonates, lithium carbonate …)

Inner part of SEI :

- Very close to carbon
- inorganic species (lithium fluoride LiF and lithium carbonate Li_2CO_3)

Figure 3. Structure of SEI at the anode of lithium-ion cells[4]

By comparison with lead-acid batteries, the aging process in standby applications is corrosion of the positive plate, or in the case of the absorbed-glass-mat (AGM) VRLA, also dryout. Lead-acid batteries do well in these applications with a proven lifetime of up to 20+ years depending upon specifications and designs.

In addition to the capacity loss resulting from aging, a lithium-ion cell is vulnerable to a substantial increase of the internal resistance which in turn may influence in a negative way the power performance of the battery. From a practical standpoint, this has a significant impact on short duration/high-rate applications. The actual increase depends on the chemistry and the aging process (Temperature and SOC) of the lithium cell. As an example, a decrease in capacity of 20% in a lithium cell can correspond to an increased DC resistance level of greater than 60%.

By way of comparison, a VLA lead-acid cell that experiences a 20% decrease in capacity, will experience an increase in the internal resistance that is 20 – 30 % lower than the lithium.

Beyond the challenge with the negative influence of the SOC, another key question remains: can we accurately predict the lifetime for the lithium-ion technology?

Due to the dynamic development in the lithium-ion chemistry, in general no one cell may exist in the same combination of active material of the anode/cathode and electrolyte for longer than 3 or 4 years. From a practical standpoint it is very challenging to predict the lifetime of the lithium cell. The additives in the electrolyte reside as a given percentage inside the organic electrolyte. As shown in Figure 4**,** the aging performance can show an extreme constant aging rate with a slow decrease of the capacity, or it can be influenced by the expiring reservoir of the electrolyte additives (page 215 et seqq) leading to unpredictable capacity drops (see Figure 5[2]).

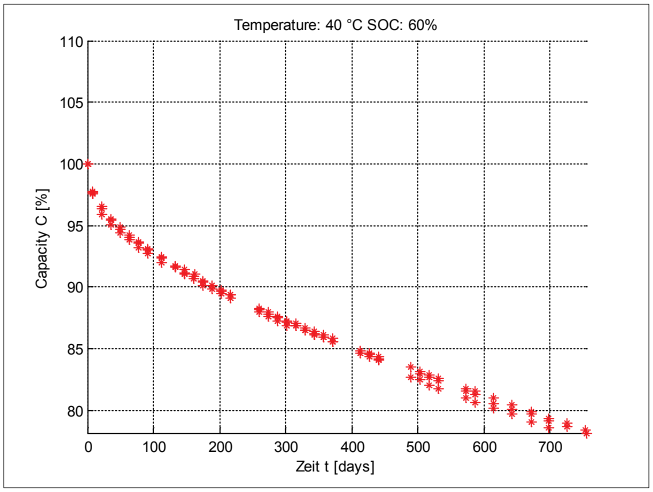
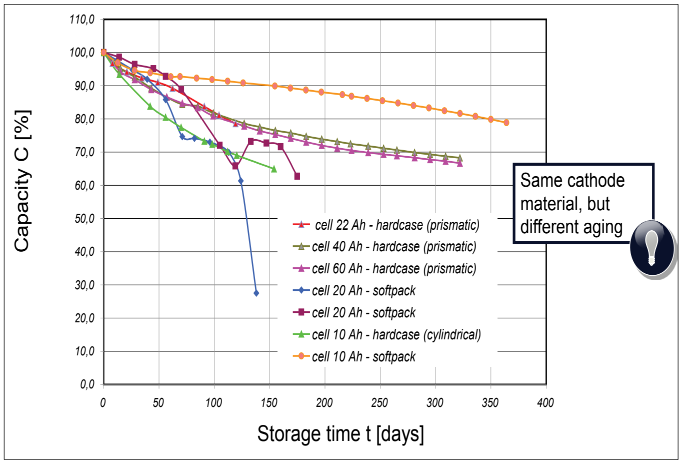


Figure 4. Aging behavior of Lithium-ion industrial cell at Temperature 40°C/60% SOC



Same cathode material, but different aging

Figure 5. Calendar aging (at 60°C and SOC 60 %) same cathode materials (LFP)[2]

The suitability of the single cathode chemistries for high-power performance is different. In a lead-acid battery the high power performance is mainly driven by the Ah rating of the battery and by the design of the electrode.

The lithium-ion cell is influenced by the chemistry of the cathode and the thickness of the active mass layer. Driven especially by hybrid electric vehicles, both Plug-in Hybrid Electric Vehicles(PHEV) and Range Extended Hybrid Electric Vehicle (REHEV), where the acceleration and recuperation power is highly important, the lithium-ion cells can perform up to 50 C (50 x nominal capacity).

For example, an ultra-high power cell of 5 Ah nominal capacity is able to provide up to 250 Amps of charge/discharge current but at a lower level of energy density. In general, for small (up to 50 kVA) UPS applications, lithium-ion technology can provide an alternative for the UPS market. However, the price/performance relationship argues against the lithium-ion cell compared to a lead-acid cell of the right type, e.g. a gelled electrolyte with proven performance in UPS applications.

Renewable Energy (RE) and Energy Storage (ESS)

Separate from the traditional standby applications we need to understand the new paradigm of renewables into the electric grid. The advantage of lithium-ion technology is the performance with the daily charge and discharge at deep cycles. Due to the intercalation process (electrolyte is not a part of the chemical reaction in relationship to the lead-acid technology) lithium-ion batteries can perform better than a lead-acid battery in this respect. It is mainly driven by the experience of the manufacturer. Note the various end-of-life scenarios for different lithium-ion types of batteries in Figure 6.

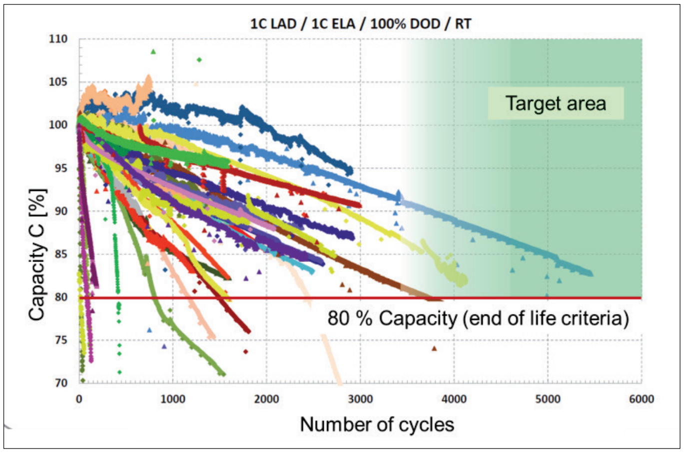


Figure 6. Lithium-ion Battery cycling (Source: KIT University of Karlsruhe)

Certain lithium-ion cells can perform 4000–5000 cycles at 100 % depth of discharge (DOD) or even more with the lithium titanate (LTO) anode material. In a deep cycling application lithium-ion technology stands out front as long as the manufacturer has a successful track record of experience with the production of long cycle durability cells. When daily discharges greater than 50 % DOD are required, lead-acid will not do as well as the lithium-ion. This is mainly due to conversion of the active mass during the charge and discharge reaction and the corresponding active mass softening while the charge/discharge process takes place. This does not occur with the lithium-ion cell.

That means for solar systems with smaller capacities (like at-home solar rooftops) lithium-ion technology may easily fulfil the demand at an interesting price point when the DOD and the potential better cycle lifetime is taken into account. It should be noted that a lead-acid battery using a tubular plate design (VLA or gelled electrolyte VRLA) can be a good alternative if the DOD is limited to a maximum of 50%.

In certain Energy Storage System (ESS) applications both the lead-acid and lithium-ion battery can play a solid role, especially for areas where 1-3MWh of energy is required. For example, in frequency regulation applications where the availability of power is required for short periods to ensure stability of the power flow on the grid, lead-acid batteries as well as lithium-ion technologies are well suited for these applications where short time durations are required (see Figure 7).

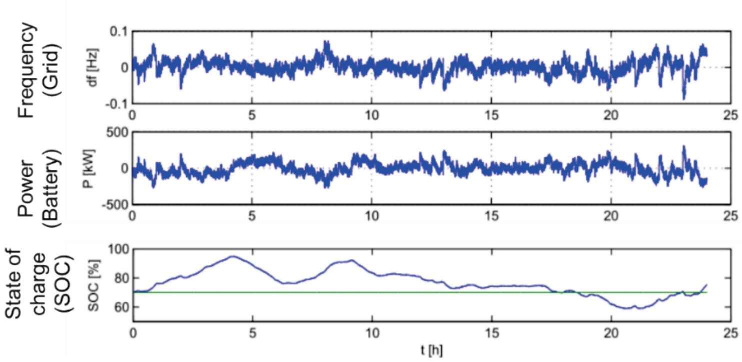


Figure 7. Typical profiles for Frequency, battery power demand and SOC

In Germany, the installation of power generation from renewables has led to serious problems in the regulation of voltage and frequency with unpredictable introduction of both demand for and supply of power into the grid. Thus, storage of this energy is needed when in oversupply and then instantaneously needed when the supply is gone. Lead-acid tubular and lithium-ion batteries are being used in many instances to handle this requirement due to the reduced cost and capacity requirements.

BAE has engaged in a partnership with Belectric, an international renewables and energy storage integrator headquartered in Germany, to provide a containerized Battery Energy Storage solution in Kitzingen, Germany. Used originally as a pilot, it is now going into commercial operation and Belectric is engaged in installing these in multiple sites throughout Europe. What this example shows is that with the reduction of the depth of discharge to approximately 15% or 30% DOD, tubular lead-acid batteries can present a solid, lower cost business case while providing a predicted 10-years or more of solid duty-cycle performance.

There are many other interesting alternatives on the way, especially if we talk about seasonal storage by power to heat or power to gas. Meanwhile, it should be understood that such energy market requirements need standards and regulation. An electrochemical storage installation can be extremely expensive if we talk about pure energy storage, and the business case for many of these alternatives will take time to justify.

Operation and Other Considerations

Lithium-ion batteries are limited in their operational temperature range. 10-30°C is the most applicable temperature range[3]. Higher temperature can influence the aging speed in a similar manner to lead-acid batteries. At lower temperature, the risk of overcharging the cells can lead to the batteries becoming unusable[4].

Sulphuric acid based lead-acid batteries are influenced at lower temperatures by the internal resistance of the acid. The charging behavior can be positively influenced by adaption of the charging voltage or additives to the active mass and/or electrolyte.

By comparison, lithium-ion cells can demonstrate a negative charging behavior due to the nature of the organic electrolyte. This can result in an increase of internal resistance that is several times faster in comparison to lead-acid batteries. The resulting adjustment of the performance is very challenging and has not been totally solved. An adaption to the charging behavior by voltage adjustment may lead to accelerated aging and is normally counterproductive.

An operation with high currents below 10°C may lead to irreversible capacity loss, driven by lithium plating at the anode and possible development of dendrites which can lead to the danger of a short circuit inside the cell. Figure 8 shows the potential rise in internal resistance within a 5.9Ah rated lithium softpack battery as the state of charge is lowered down to 10% SOC.

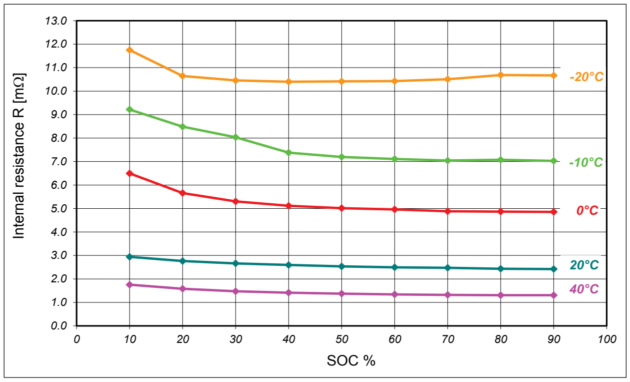


Figure 8. Development of DC resistance on dependence on state of charge high power Lithium-ion cell (5.9 Ah softpack)

An alternative solution is to actively derate the cells. However, this reduces the universal applicability of the systems. A thermal management system is also required for most industrial/commercial applications which adds to cost and reduces system efficiency.

The safety for lithium-ion batteries is mainly defined by the electrolyte (organic electrolyte with the burn behavior like alcohol) and the cathode material. There are two main problems to discuss with regard to the safety of lithium-ion cells: 1) production quality and created short circuits in case of production failure and 2) operation of the batteries at different ambient temperatures outside the permissible voltage ranges. Both of these critical points may lead to an ignition of the electrolyte[5].

The electrolyte is transferring the energy content/heat to the cathode material. Therefore, the main question becomes which of the cathode materials is installed in the cell. In the case of lithium-iron-phosphate (LFP) the limit of uncontrolled energy output is really set by the thermal behavior of the LFP material. The complete opposite is the case with lithium cobalt oxide ($LiCoO_2$) which offers the best energy content but remains very challenging with regard to the thermal aspects with a high tendency for overheating.

Figure 9 graphs the resultant thermal behavior of various cathode materials at various temperature levels.

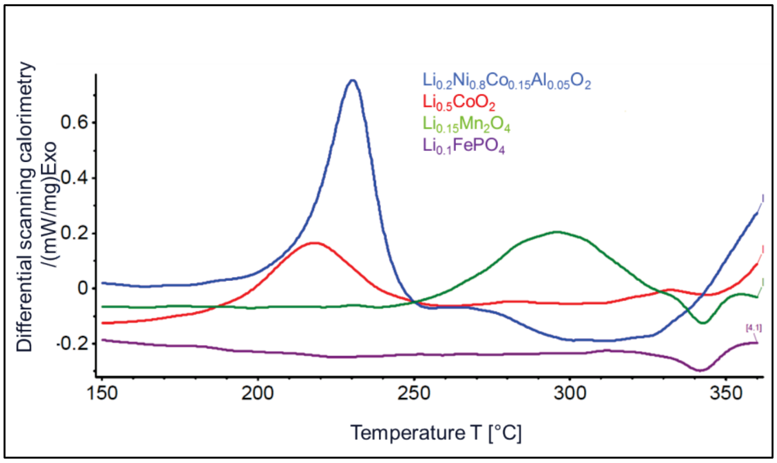


Figure 9. Cathode material thermal behavior (Source: ZSW)

Therefore, a sufficient control of the battery's operational conditions as well as an operation strategy is essential, and must be realized by the on-board electronics.

Additionally, the transport of lithium-ion cells can be challenging. Before the cells/system are approved, a safety test must be performed at both an individual cell and system level. UN transport testing requirements include altitude simulation, thermal test, vibration, shock, external short circuit, impact, overcharge and forced discharge. However, all these tests are required for standard commercial transportation. Not foreseen is the transport of damaged cells with electrolyte leakage. In Europe universal standards have not yet been instituted, and so the transport of damaged cells is carried out by individual solutions. Some examples are [1] storage of the battery for a minimum of 14 days, [2] covering by vermiculite and cooling of batteries with dry ice which is very costly and requires a lot of time-consuming labor effort.

Recycling

Currently, lithium-ion batteries are generally recycled like consumer and cellular phone batteries. The major focus during the recycling process is the conductive electrode material (copper) and cell container (steel), as well as the active material (nickel and cobalt). Cobalt, like nickel and lead are mainly driven by the material prices for those metals when it comes to recycling. Lithium, however, drops mostly as a slag and is added at best case as a concrete additive hardener for cement or is processed in the glass industry. Realistically, a traditional recycling for the lithium-ion battery industry does not exist. Therefore, in the case of lithium recycling, it can't be spoken about as a closed raw-material recirculation. The recycling process itself (metallurgical or electro-chemical) is not cost neutral and the cost cannot be fully covered by the recovered materials from the lithium-ion cells.

Due to the ambitious plans of the automobile industry for electric mobility (BEV, PHEV), we should not lose sight of the fact that the lithium raw material is the most important raw material for future demand. In view of the chronicled uncertainty of lithium supply and the lack of optimized recycling procedures, energy storage cases above 1 kWh may remain a challenge for the future. What is needed is to develop new recycling procedures (e.g., wet-chemical procedures) in order to secure the future of lithium based energy storage.

Further, it is very challenging to define one single basis for the recycling process due to the different cell chemistries of lithium-ion cells. In each case an individual solution has to be agreed upon between the customer and recycling partner (see Figure 10) to find a reasonable recycling process that focuses on the materials requirements while at the end reduces the price for the processing.

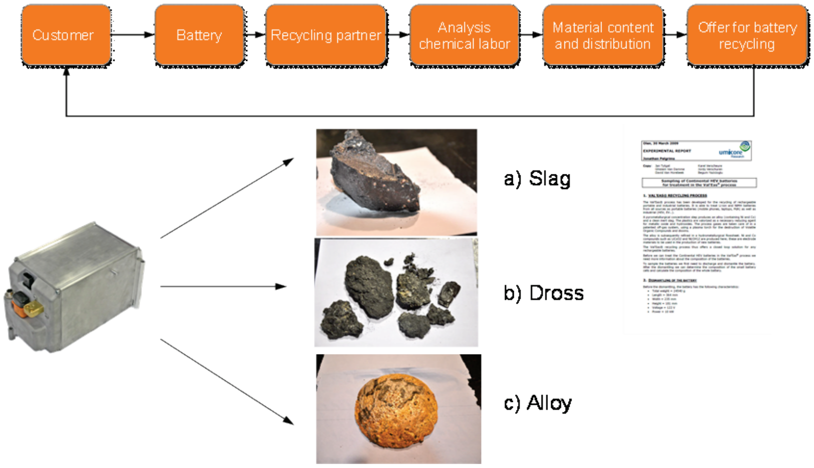


Figure 10. Recycling process for lithium-ion batteries

Summary

The following tables 1a and 1b provide a comparison of the advantages and disadvantages of both battery types for commercial and industrial applications (excluding consumer electronics):

ADVANTAGES	**DISADVANTAGES**
Lead-Acid Batteries	**Lead-Acid Batteries**
• Proven technology – over 100 years	• Maintenance required to ensure batteries perform to expected life
• Cost-effective for traditional standby applications	• Requires more floor space to install an equivalent Ah or kWh Li-Ion string
• Ease of installation – no battery management control system required	
• Good cycle count with tubular and gelled-electrolyte cells	
• Published standards and best practices exist	

Table 1a. Comparison of Advantages/Disadvantages of both Li-Ion and Lead-Acid Cells[5]

ADVANTAGES	**DISADVANTAGES**
Li-Ion Batteries:	**Li-Ion Batteries:**
• No manual maintenance required	• No manual maintenance permitted – requires Battery Management System (BMS)
• Good cycling life – discharges up to 100% of capacity; 4000 cycles with some Li-Ion designs	• Safety concerns: fires and thermal runaway – includes capacity loss and potential for thermal runaway when overcharged
• High specific energy and energy density	• Higher initial cost for traditional standby applications
• High rate discharge capability	• Degrades at high temperature
• Low self-discharge rate	• Becomes unsafe in extreme cold temperatures
• Fast recharge capability	• Additional effort for recycling necessary
	• Relatively new in industrial standby applications – technology is less than 25-years old
	• No solution yet regarding damaged batteries (electrolyte leakage)
	• Published safety standards and best practice guidelines do not currently exist

Table 1b. Comparison of Advantages/Disadvantages of both Li-Ion and Lead-Acid Cells[5]

Conclusion

Lithium-ion technology is certainly a well-established technology for mobile technology including EV and PHEV/REHEV. It now seeks to enter the market for traditional standby industrial applications, driven in large part as a means to recover the very large investments made in plant infrastructure.

However, for traditional standby applications with a moderate cycle requirement, lead-acid batteries remain a very effective cost-benefit solution, especially for sites where installation space is not a major limitation or where high volume is not required for discharges at the mains. Lead-acid is a proven system with over 100 years of evolutionary experience and their initial installation costs are reasonable.

For applications where a high daily energy throughput is needed and duration periods are not excessive, lithium-ion technology can exist on a par with lead-acid batteries. For home solar systems, it can be a very effective alternative. For industrial applications, however, like behind-the-meter systems in hospitals, universities and business parks as well as for electric utility protection and control systems, lead-acid is still a most attractive and very cost-effective solution.

For smart grid and utility scale applications the situation is divided. Both types of batteries are in various stages of pilot or commercial operation. Attention will continue to focus on improving the predicted lifetimes for lithium-ion technologies. However, even with the limitations of maximum depth of discharge lead-acid can still be considered a good alternative with a faster breakeven scenario when looked at as a business case for cost purposes.

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