Contents lists available at ScienceDirect

Journal of Energy Storage

journal homepage: www.elsevier.com/locate/est

Lead batteries for utility energy storage: A review

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ARTICLE INFO

Article history: Received 10 October 2017 Received in revised form 8 November 2017 Accepted 9 November 2017 Available online 15 November 2017

Keywords: Energy storage system Lead-acid batteries Renewable energy storage Utility storage systems Electricity networks

ABSTRACT

Energy storage using batteries is accepted as one of the most important and efficient ways of stabilising electricity networks and there are a variety of different battery chemistries that may be used. Lead batteries are very well established both for automotive and industrial applications and have been successfully applied for utility energy storage but there are a range of competing technologies including Li-ion, sodium-sulfur and flow batteries that are used for energy storage. The technology for lead batteries and how they can be better adapted for energy storage applications is described. Lead batteries are capable of long cycle and calendar lives and have been developed in recent years to have much longer cycle lives compared to 20 years ago in conditions where the battery is not routinely returned to a fully charged condition. Li-ion batteries have advantages in terms of energy density and specific energy but this is less important for static installations. The other technical features of Li-ion and other types of battery are discussed in relation to lead batteries. A selection of larger lead battery energy storage installations are analysed and lessons learned identified. Lead is the most efficiently recycled commodity metal and lead batteries being collected and recycled in Europe and USA. The sustainability of lead batteries is compared with other chemistries.

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https://doi.org/10.1016/j.est.2017.11.008

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1. Introduction

The need for energy storage in electricity networks is becoming increasingly important as more generating capacity uses renewable energy sources which are intrinsically intermittent. The spinning reserve of large networks is becoming less able to maintain power quality with increased renewable inputs and the strategies needed to optimise renewable input without curtailment or other measures are driving a move to energy storage. Electrochemical energy storage in batteries is attractive because it is compact, easy to deploy, economical and provides virtually instant response both to input from the battery and output from the network to the battery. There are a range of battery chemistries that can be used and lead batteries offer a reliable, cost-effective solution which can be adapted for different types of energy storage applications [1–6].

Lead-acid batteries are supplied by a large, well-established, worldwide supplier base and have the largest market share for rechargeable batteries both in terms of sales value and MWh of production. The largest market is for automotive batteries with a turnover of \sim \$25BN and the second market is for industrial batteries for standby and motive power with a turnover in 2015 of \sim \$10BN. The majority of industrial batteries are used for standby applications to provide secure power for telecommunications, data networks, national security, and a huge range of applications where continuity of the electricity supply is essential. Energy storage is an extension of standby or stationary service but the application requirements are quite different and as the market for energy storage grows, it needs to be recognised as a fully separate market sector [7].

In the very early days of the development of public electricity networks, low voltage DC power was distributed to local communities in large cities and lead–acid batteries were used to

provide peak power and short term energy storage. DC distribution was soon displaced by AC systems and the ability to use transformers to step-up or step-down the voltage allowed large area networks to be developed. The use of battery energy storage systems (BESSs) rapidly diminished as networks grew in size. Stability is achieved by careful management of the network with generation being balanced with consumption. The AC frequency is permitted to vary within narrow limits as higher overall loads reduce the frequency and voltage settings may be changed to adjust demand slightly but the main method of control is spinning reserve where an unloaded generator that is synchronised with the grid can be brought into use very quickly. This could be hydroelectric generators. Rapid reserve differs from spinning reserve in so far as the energy source does not have to already be synchronised with the grid. BESSs fall into this category as the DC battery output can be converted to AC with solid-state power conversion equipment and systems brought on line almost instantaneously. Over time power quality in terms of reliability, frequency stability, voltage and volt-ampere reactive (VAR) control has become more critical. Large networks have installed pumped hydro-electric energy storage schemes to augment their spinning reserve but as renewable energy sources have become more important a higher level of rapid reserve is required. Batteries can provide this with lead batteries offering high efficiencies for short time reserve and their use for grid support, smart grids, local systems and home and small commercial energy systems will increase [8].

Advanced lead batteries have been used in many systems for utility and smaller scale domestic and commercial energy storage applications. The term advanced or carbon-enhanced (LC) lead batteries is used because in addition to standard lead-acid batteries, in the last two decades, devices with an integral supercapacitor function have been developed. These may have a negative electrode with a combined lead-acid negative and a carbon-based supercapacitor negative (the UltraBattery ® and others) or they may have a supercapacitor only negative (the PbC battery), or carbon powder additives to the negative active material. In all cases the positive electrode is the same as in a conventional lead-acid battery. Lead-acid batteries may be flooded or sealed valve-regulated (VRLA) types and the grids may be in the form of flat pasted plates or tubular plates. The various constructions have different technical performance and can be adapted to particular duty cycles. Batteries with tubular plates offer long deep cycle lives. For use with renewable energy sources, especially solar photo-voltaic (PV) sources, the pattern of use is for regular discharges with the battery not necessarily being returned routinely to a full state-of-charge. This partial state-ofcharge (PSoC) operation can be damaging for lead-acid batteries as it leads to irreversible sulfation of the negative plates and methods to overcome this problem have been the subject of intensive development [9,10].

Sustainability is one of the most important aspects of any technology and lead batteries are no exception. Recycling of leadacid batteries has been an established practice since they were first used and is continuing to increase. Recycling rates approach 100% in Western countries and very high rates are achieved elsewhere. Batteries use 85% of the lead produced worldwide and recycled lead represents 60% of total lead production. Lead-acid batteries are easily broken so that lead-containing components may be separated from plastic containers and acid, all of which can be recovered. Almost complete recovery and re-use of materials can be achieved with a relatively low energy input to the processes while lead emissions are maintained within the low limits required by environmental regulations. Scrap prices are such that recycling proceeds efficiently and economically. This is in contrast to other battery chemistries, especially Li-ion, where recycling rates are much lower, processes need to become more efficient, collection and separation needs to be developed and the economics are not favourable.

2. Lead battery technology

2.1. Lead-acid battery principles

The overall discharge reaction in a lead-acid battery is:

$$PbO_2 + Pb + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O \tag{1}$$

The nominal cell voltage is relatively high at 2.05 V. The positive active material is highly porous lead dioxide and the negative active material is finely divided lead. The electrolyte is dilute aqueous sulphuric acid which takes part in the discharge process. On discharge HSO₄⁻ ions migrate to the negative electrode and produce H⁺ ions and lead sulfate. At the positive electrode lead dioxide reacts with the electrolyte to form lead sulfate crystals and water. Both electrodes are discharged to lead sulfate which is a poor conductor and the electrolyte is progressively diluted as the discharge proceeds (Fig. 1). On charge the reverse reactions take place. As cells approach top-of-charge and the electrodes have been progressively converted back to lead dioxide and lead, the specific gravity of the electrolyte rises as the sulfate concentration is increased. Further charging will result in water loss as it is electrolysed to hydrogen and oxygen but the over-potential at which this occurs is sufficiently high for water loss to be manageable by controlling the charging voltage. For flooded batteries, correct selection of the grid alloys and charging parameters reduce water loss to very low levels so that adding water for battery maintenance only needs to be carried out occasionally. If, however, a sealed cell is designed so that the



$Pb + PbO_2 + 2H_2SO_4 \rightleftharpoons 2PbSO_4 + 2H_2O$

Fig. 1. Chemistry and principal components of a lead-acid battery.

electrolyte is immobilised in either an absorptive glass mat (AGM) separator or gelled with finely dispersed silica, channels can be formed between the positive and negative plates, either as connected gas porosity in AGM types or micro-cracks in the gel such that there is a passage for oxygen gas from the positive where it is generated to the negative where it reacts with lead to form lead sulfate. The reactions are:

$$H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^- and$$
 (2)

$$Pb + \frac{1}{2}O_2 + H_2SO_4 \rightarrow PbSO_4 + H_2O$$
 (3)

Diffusion of oxygen from the positive to the negative in the gas phase is much faster than in liquid electrolyte. Oxygen is chemically recombined to produce lead sulfate which is the normal discharge product, depolarising the plate, which is then recharged back to lead as in the normal charge process. Other requirements for sealed recombinant cells are to select the grid alloys with a high hydrogen over-potential to reduce hydrogen evolution at the negative and more generally to have high purity materials for both active materials and grids. In addition, cells need to have one-way valves to permit the release of small quantities of hydrogen and prevent air from entering cells. Batteries with such cells are referred to as valve-regulated lead-acid cells as they have a one-way valve to release gas from the cell at a pre-determined internal pressure but prevent air entering the cell from the surroundings.

2.2. Cell construction

Lead-acid cells are constructed from lead alloy grids which mechanically support the positive and negative active materials and act as current collectors. The grids are stacked together as positive and negative plates and interleaved with a porous electrically insulating separator. The plate stack is inserted into a suitable moulded polymer case to contain the cell components and the electrolyte with the positive and negative plates connected together, terminals, a lid and venting arrangements. There are two main types of positive plate; flat pasted plates and tubular plates. The negative plates are always flat pasted types. There are also spiral wound plate types and bipolar designs but these tend to be confined to smaller capacities. In addition to the different plate types, cells may be flooded or VRLA types.

For pasted plates, the grids may be cast, made by slitting and expanding sheets of lead alloy or by punching sheets of lead alloy. The lead alloy may contain antimony in varying quantities, it may be alloyed with calcium and tin and other elements or it may be pure lead with very small alloying additions often including tin. Alloys with antimony are used for the positive grids of flooded cells designed for deep cycle applications. Alloys with calcium and tin and also pure lead are used for the positive grids of VRLA cells. Different alloys with lower antimony levels may be used for negative grids for deep cycle service. For some types of flooded cell allovs with calcium and lower levels of tin are used for negative grids and these allovs are used for VRLA cells. The active materials are applied to the grids in the form of a porous paste formulated from lead oxide and sulphuric acid. During paste mixing basic lead sulfates are developed. These have a robust, interlocking structure which is well bonded to the grids. The pasted plates are then processed in hot humid conditions (curing) so that the paste particles become strongly bonded to each other and the grid surfaces. The basic lead sulfates are then converted to lead dioxide and lead by an electrochemical formation process. The positive active material may contain minor additives or strengthening fibres but the negative active material has specific additives of barium sulfate, lignosulfonates, carbon black as expanders as well as fibres. These maintain the microporous and conductive structure of the negative active mass in service to improve lowtemperature performance and cycle life.

For a flooded pasted plate cell, the separator may be microporous polyethylene, polyvinyl chloride (PVC), rubber or other materials. The requirement is high porosity to allow sufficient acid to be available for ionic conductivity and as active material with a level of tortuosity to prevent penetration of the separator by lead. The positive plate needs to be protected against loss of active material on cycling. This may be simply by a sheet of glass fibre mat attached to the separator and pressed against the positive plates or a more elaborate arrangement where glass mats and scrims are wrapped around the positive plates and held in compression by a perforated polymer sheet.

For a VRLA pasted plate cell, AGM separators are used. These are made from glass microfibers by a paper-making process and provide separation between the plates as in a flooded battery but fully absorb the acid and also allow a network of connected empty pores to be developed which have no acid, this allowing oxygen diffusion in the gas phase. It is also possible to use gelled electrolyte in pasted plate cells and in this case microporous plastic separators need to be used but the specification needs to be aligned to this type of cell.

In pasted plate cells, either flooded or VRLA, the positive active material needs to have sufficient density and structure to provide durability on cycling. The charge and discharge processes are reconstructive transformations involving changes in volume and shape and so a high integrity is essential. This is achieved in the paste formulation and in the curing and drying stage after pasting where conditions of higher temperatures and humidity favour the formation of tetra-basic lead sulfates which provide better cyclic performance. The correct conditions in curing also ensure that the active material is well-bonded to the grids and that the interface between the active material and the grid is fully conductive. Red lead (Pb₃O₄) may be added to the paste formulation which improves the efficiency of formation and the structure of the positive active mass. Phosphoric acid (H₃PO₄) may be added to the positive active material. This increases the adhesion between the positive active material and the grids and the cohesion of the active material.

Tubular positive plates have the grid in the form of a series of spines attached to a top bar rather like an elongated comb. This is made by a die casting process using the same range of alloys as for pasted plate grids. The spines are surrounded by tubes made from woven or non-woven glass or polyester fibre which serve to retain the active material. The tubes are usually in the form of an array which fits over the spine and seals to a small wider part at the top. The annulus between the spine and the tube is filled with the active material either as lead oxide or red lead powder or a paste or a slurry of the same materials and the bottom of the annulus sealed with a plastic closure. The plates are then soaked or treated in acid to convert the oxides to lead sulfate, dried and then assembled into cells which are then formed electrochemically. The same considerations as for pasted positive plates for the structure and density of the positive active mass apply to tubular plates although high temperature curing is not used. The same types of separators as for flooded and gel pasted plate VRLA cells are suitable. VRLA AGM variants of tubular plate cells are not used commercially. Tubular plates have excellent behaviour in respect of the retention of active material because the tubes are very robust and do not allow shedding to occur.

2.3. New developments

2.3.1. Carbon-enhanced designs

The adoption of stop and start or micro-hybrid technology by the automotive industry to improve fuel economy and to reduce tailpipe emissions has necessitated a search for ways of improving the behaviour of lead-acid batteries where instead of a single engine starting event at the start of a journey, there are a large number of engine starts and the battery undergoes shallow cycling on a continuous basis. This mode of operation is referred to as highrate partial-state-of-charge (HRPSoC) duty and battery performance reduces after a period in service unless the battery is adapted for this mode of operation. The cause of the reduction is a failure of the negative plate to accept charge because the charge and discharge reaction of the negative plate is not fully reversible and lead sulfate becomes difficult to fully charge, it gets accumulated on cycling and inhibits plate operation. The problem is exacerbated as the battery is not routinely brought to top-ofcharge because in order to accept charge and recover energy it cannot be fully charged. A large research effort in the industry has, however, led to new designs of battery, both flooded and VRLA, that are able to meet the requirements. The key to this has been the development of special carbons that improve the behaviour of the negative plates. Similar problems exist with energy storage systems, especially with solar PV and grid support systems and many of the solutions that have been researched for automotive batteries can be further developed for industrial batteries [11–13].

There are a number of ways in which carbon can modify the performance of the negative plate of a lead-acid battery. These are; (i) by capacitive effects, (ii) by extending the surface area on which the electrochemical charge and discharge processes take place and (iii) by physical processes. Capacitative effects (i) are favoured by carbons that have large specific surface areas and are in good contact with the grid as the current collector and the spongy lead matrix of the active mass. The carbon does not, however, need to be intimately mixed with the sponge lead. For surface area effects (ii) the carbon is also required to be conductive and in contact with the current collector but since the carbon promotes bulk rather than surface processes, the surface area can be less than the capacitative process. Where carbon is used to take advantage of physical processes (iii) it does not have to be conductive but it does have to be very intimately mixed with the sponge lead and the particle size sufficient for its function not to be reduced over time. To the extent that these requirements are conflicting and because there are a huge variety of different carbon materials a lot of research has been directed at optimising combinations of different carbons but much basic work remains to be done to elucidate the fundamental mechanisms [11]. This will lead to further improvements in lead batteries for energy storage applications.

2.3.2. Carbon negative current collectors

It is possible to replace some or all of the metallic parts of the negative grid with carbon. Various concepts have been studied both with rigid carbon foams, lead electroplated graphite foil and flexible carbon felts. The rigid carbon foams had outstanding life and active mass utilization [14] but the brittle nature of these materials made manufacture problematic. Lead electroplated graphite foil had a low level of utilisation but high durability in PSoC cycling suggesting that lead sulfate formation was inhibited [15]. A more promising concept has been developed by ArcActive in New Zealand in which the lead grid has been replaced with a carbon felt activated by treatment with an electric arc under controlled conditions [16]. The felt is impregnated with active material and attached to lead alloy current collectors. This construction shows excellent behaviour in PSoC operation. To date it has been developed for automotive applications but it has good potential for energy storage applications in larger formats especially as the high rate capability required for automotive service is not critical for most energy storage duty cycles.

2.3.3. Carbon negative electrodes

It is possible to substitute the negative active material entirely with carbon in which case the electrode has no Faradaic energy storage but functions as a capacitor and with carbon materials with suitable physical form and high specific surface area the electrode becomes a supercapacitor. This can be paired with a conventional lead dioxide positive plate to make an asymmetric supercapacitor. The energy density of this type of device is low compared to a leadacid battery and it has a much more steeply sloping discharge curve but it offers a very long cycle life. It can also be recharged rapidly. This concept has been developed by Axion Power in the USA as an energy storage system [17–19].

2.3.4. Supercapacitor/battery hybrids

It is also possible to have a composite negative electrode with a carbon-based supercapacitor combined with a conventional negative electrode and when this is used with a standard positive electrode this hybrid construction offers substantially improved behaviour in shallow cycling. The two components of the negative electrode are connected together in parallel and the capacitor part of the electrode acts as a buffer to share current with the negative plate and reduce the rate of charge and discharge. This is available commercially as the UltraBattery® and offers important advantages over both conventional lead-acid batteries and asymmetric lead-based supercapacitors [20,21]. These are: (i) the avoidance of irreversible sulfation of the negative plate in PSoC cycling and the need for intermittent conditioning cycles where the battery is charged for an extended period; (ii) improved high-rate charge acceptance; (iii) better self-balancing of cells in series strings; and (iv) an energy density and voltage profile on discharge in line with a lead-acid battery.

2.3.5. Bipolar lead-acid batteries

Bipolar constructions have been researched over many years and more recently a number of concepts are showing greater promise of technical and commercial success. In a bipolar battery, apart from the end-plates, the plates have one side operating as the positive and the other as the negative separated by a membrane that is impervious, electronically conductive and corrosion resistant. For lead-acid batteries selection of the membrane is the key and the other issue is to have reliable edge seals around the membrane with the electrodes on either side. The use of porous alumina impregnated with lead has been trialled without success. Conductive titanium suboxides (Ebonex) incorporated in resin fabricated into thin sheets have been extensively examined by Atraverda but have not been commercialised. Ebonex has reasonable electronic conductivity and is inert in a lead-acid cell environment but as a membrane, the resistance is relatively high [22]. Silicon is also a candidate and although it is a semiconductor, it can be made sufficiently conductive to operate as a membrane in a bipolar lead-acid battery. This concept is being developed by Gridtential in the USA [23,24]. The use of polymer sheets made conductive with metallic fibres is under study by Electriplast in the USA but no battery performance data has been published [25]. Lead sheet is an excellent membrane provided that it is sufficiently corrosion resistant and Advanced Battery Concepts have a design which uses a polymer support for lead sheet. Battery performance data for this design show good results [26,27]. A successful bipolar lead-acid design would offer an attractive energy storage battery.

3. Durability limiting factors of lead-acid batteries in utility service

The failure modes of lead-acid batteries are generally as follows [28,29]:

3.1. Positive grid corrosion

The positive grid is held at the charging voltage, immersed in sulfuric acid, and will corrode throughout the life of the battery when the top-of-charge voltage is reached. The grid alloy, either lead-antimony, lead-calcium-tin, lead-tin or pure lead, is selected to have a high corrosion resistance, and the grid thickness and other grid design parameters are selected to provide sufficient grid metal for the expected life of the battery. The grid manufacturing process and microstructure of the grid alloy are important. Grid corrosion is accelerated by higher charging voltages. The voltage is set to achieve a fully charged battery without excessive water loss, and corrosion is kept at a level to obtain the design life. Correct setting of the charging voltage is essential. Grid corrosion is also sensitive to temperature. Grid resistance increases during the life of the battery, accelerating towards end-of-life. There will also be some loss of connectivity between the grid and active material.

3.2. Positive grid growth

Changes in active material volume and the volume of the corrosion product place stresses on the grids, which may become distorted as the battery ages. The grids can grow to contact the negative group bar and cause short circuits. They can also grow such that they are no longer insulated at the edges of the plates. Some battery designs accommodate this harmlessly by using an insulator under the group bar. Others permit the grids to grow downwards or to accommodate some distortion. It can lead to pressure on the pillar seal, which may be distorted and develop leakage. The case may become cracked and start to leak. Grid growth will also cause loss of connectivity between the grid and the active material, increasing internal resistance and reducing capacity. Grid growth may be reduced by correct selection of the grid alloy and ensuring the grid thickness and wire sections are adequate. Tubular positive plates are generally more resistant to the effects of grid growth than pasted plates as lateral growth is constrained by the fabric gauntlets and vertical growth can be accommodated by cell design. Lead-antimony alloys are more resistant to grid growth than lead-calcium-tin alloys as they have higher tensile strength and creep resistance but for VRLA batteries lead-calcium-tin, lead-tin or pure lead must be used for the grids in order to suppress water loss.

3.3. Sulfation

The normal discharge product on both the positive and negative plates is lead sulfate. This is normally very finely divided and easy to recover by recharge, but over time and on cycling it tends to coarsen and becomes more difficult to recharge, eventually leading to capacity loss. There will be an increase in the internal resistance of the cell and loss of performance. Sulfation will be increased if the battery is left in a partially or fully discharged state for extended periods and the use of carbon additives is an important method of reducing the effects of sulfation. In cyclic operation, it is important to use the correct charge voltage settings.

3.4. Active material softening

Over time the active material may become soft and less cohesive. This will be more rapid if the battery is deeply cycled and will lead to capacity loss. For positive plates it can be reduced by the use of higher density pastes, by the use of processing before formation to enhance the formation of tetrabasic lead sulfate, by the use of additives for the same purpose and by the use of inert fibres in the active material for reinforcement. It can also be mitigated by ensuring that the plates are under compression. This is particularly true for VRLA batteries.

3.5. Acid stratification

During recharge sulfuric acid is produced from both plates as lead sulfate is reduced at the negative plate and oxidised at the positive plate and acid with a higher concentration and therefore density tends to move to the bottom of the cell. The acid is stratified with a gradient of density from top to bottom of the cell. This will increase the tendency for sulfation in the areas with higher acid concentration and also results in variations in utilisation of the active material. It can be eliminated by simple acid recirculation pumps. The problem affects flooded cells and VRLA cells are less affected by stratification as the AGM separator or gel immobilises the electrolyte. For AGM types the wicking height of the separator is finite which limits the cell height and tall cells are usually operated on their side to avoid any issues of variation in acid density.

3.6. Dry out

For VRLA batteries at end-of-life or in certain fault conditions, such as excessive charging voltages, there will be a loss of water from the cells, which will lead to shrinking of the separator material, loss of compression, and reduced contact between plates and separator. These conditions result in loss of capacity and increase in internal resistance. Higher service temperatures also increase the risk of drying out. If dry out occurs more rapidly, for example as a result of a high applied voltage, it can lead to thermal runaway. It can also occur over extended periods of time at normal charging voltages but the battery would be beyond the normal service life. Cells are designed such that dry out is not a normal failure mode. Dry out may be the result of a mechanical defect, high ambient temperature, incorrect charging, a combination of these contributing factors or it may occur in a cell that is beyond end-oflife. If the charging voltage is controlled correctly dry out should not be a failure mode. For flooded batteries, there is no risk of dry out with regular maintenance water additions.

3.7. Pillar seal leakage

Pillar seals may leak in service as a result of manufacturing defects. VRLA cells may dry out and acid on the battery surface may

lead to ground fault currents which in turn may lead to overheating and thermal runaway.

3.8. Lid seal leakage

Lid seals may also leak as a result of manufacturing defects with similar results to pillar seal leakage. Good manufacturing practice is the key.

3.9. Vent failure

Vents for VRLA may be missing, ejected or fail to close leading to a run down in capacity, accelerated dry out, loss of electrolyte or both. For flooded cells no damage to the cell occurs if the vents are damaged.

3.10. Mechanical damage

Accidental mechanical damage may cause cells to leak leading to failure similar to pillar seal leakage. Loss of electrolyte may lead to dry out and loss of capacity.

3.11. Group bar corrosion

The group bar connection to the plate lugs may become corroded and possibly disconnected. The group bar alloy needs to be correctly specified and the connection between the group bar and the plate lugs needs to be carefully made, especially if this is a manual operation.

3.12. Internal shorts

These can arise from damage or penetration of the separator. They may be hard shorts leading to rapid failure or soft shorts where the defect is relatively minor and may not be initially apparent as they can develop over time. Internal shorts will cause loss of capacity by self-discharge prior to use. Shorts may lead to thermal runaway in VRLA cells.

3.13. External ignition of hydrogen

Batteries emit small quantities of hydrogen on charge. In normal operation and in a well-ventilated enclosure, this should not reach the flammable limit for hydrogen in air but under fault conditions this may occur. Flame retardant vents should be used.

3.14. Overheating of external connections

If the inter-cell or inter-monobloc connections are not secure, they may become overheated especially on discharge, because of local high resistance and in extreme cases this may result in fire.

3.15. Thermal runaway

Thermal runaway in VRLA batteries is an unstable condition where the application of the charging voltage drives the battery temperature higher in an uncontrolled manner and in extreme cases may lead to fire or to battery explosions. The current is normally not limited as the battery will be able to draw substantial currents for recharge after a discharge cycle. There are a number of causes of thermal runaway as indicated. Dry-out, internal shorts, cell reversal and other defects may result in thermal runaway. It can also be caused by excessive charging voltage and it will be accelerated by increased temperatures in the local environment. For flooded cells there is no difficulty.

3.16. Designs for longer life

The key to lower lifetime costs for lead batteries in energy storage applications is longer life under all operating conditions. Some of the failure modes described can be avoided by best practice in battery design, manufacture and operation but others including positive grid corrosion and growth, sulfation and active material softening need a combination of better materials, further refinements in battery design and careful control of the charging parameters.

4. Position of lead batteries in comparison to other energy storage systems

4.1. Non-battery energy storage

Pumped Hydroelectric Storage (PHS) is widely used for electrical energy storage (EES) and has the largest installed capacity [30–34]. The principle is simple; water is pumped to a high reservoir during off-peak demand hours and is released to a low reservoir during peak hours powering water turbines driving generators to produce electricity. Plant sizes range from a few MW to low GW power capability. Efficiency is in the range from 70 to 85% overall and installations may last more than 50 years with suitable maintenance. PHS is used for time shifting, for frequency control and for supply reserve. Deployment of PHS schemes is restricted by geography and they tend to require long construction times as well as significant capital investment.

Compressed Air Energy Storage (CAES) is used for EES in large installation with capacities up to 300 MW for a few hours [35–37]. At times of low demand, air is compressed and stored in suitable tanks or naturally occurring underground caverns and at peak times, used to drive turbines and generate electricity. Heat recovery systems are used to recover energy on compression and to heat the air as it is expanded in order to increase efficiency. Larger systems require underground caverns that are seismically stable which are not widely available. Operating times are typically a few hours and efficiencies are only moderate.

Flywheel Energy Storage (FES) uses a flywheel to store mechanical energy which is converted into electrical energy output by a generator/motor unit that also serves to input mechanical energy to the flywheel by using electricity to drive the unit as a motor. Efficiencies are reasonably high (90–95%) and the response time is very short (milliseconds) but the energy density is low. As a result, it is suitable for very short time duty cycles and in particular for frequency regulation [38–40].

Other storage technologies are possible including supercapacitors, thermal energy storage, superconducting magnetic energy storage and hydrogen storage with fuel cell generation. They all have limitations which are discussed elsewhere [2]. Batteries are attractive because they are easy to deploy and can be installed on many utility sites in a modular fashion with reliable equipment for power conversion. EES with batteries has good overall efficiency, they can be installed with short lead-times and can provide power on demand without delay.

4.2. Comparison with other battery chemistries

4.2.1. Lithium-ion

Li-ion batteries store electrical energy in positive electrode materials made of lithium compounds capable of reversible intercalation of Li ions and negative electrode materials made of carbon or

graphite that can accommodate Li in the solid state [41–43]. Non-aqueous electrolytes are used as Li reacts violently with water. These are a mixture of ionisable organic solvents such as propylene carbonate with suitable lithium salts in solution. The separators are microporous plastic films which may be coated with ceramic particles to enhance the safety of the cells (Fig. 2).

For consumer cells, lithium cobaltite (LCO) is widely used as the positive electrode material but this is expensive and for BESS applications lower cost alternatives are used. These include mixed oxides of nickel, cobalt and aluminium (NCA), nickel, cobalt and manganese (NCM) in which the cobalt content is diluted. Lithium manganese dioxide spinel (LMO) and lithium iron phosphate (LFP) have also been used to reduce costs. For the anode, graphite or carbon is generally used but silicon is being studied and lithium titanate (LTO) can be used. The keys to wider deployment for BESS are longer cycle life and lower costs. The use of Li-ion batteries in electric vehicles is driving costs downwards.

Safety needs to be carefully considered for Li-ion cells. They have a high energy density and the organic electrolyte is flammable. Thermal runaway is a risk and the materials selected, cell and battery construction and charging systems need to be carefully specified to ensure in service problems are minimised. Battery monitoring systems with thermal sensors, voltage and current measurement and fuses are used for safe operation.

4.2.2. Sodium-Sulfur

Na-S batteries have molten liquid sodium and sulfur as the electrode materials and operate at high temperatures between 300° and 350 °C to keep the electrodes in liquid form and achieve good ionic conductivity in the electrolyte, which is a solid ceramic material [44-46]. The electrolyte is beta-alumina (β -Al₂O₃), which conducts sodium ions at the operating temperature. Sodium and sulfur react on discharge to form sodium polysulfide. The energy density is substantially higher than lead-acid batteries and they have a long cycle life. Safety is an important issue and careful design is required to prevent cell failures from propagating. Na-S batteries are manufactured from cheap and plentiful raw materials but the manufacturing processes and the need for insulation, heating and thermal management make these batteries quite expensive. They are also more economical in large units as thermal management of small batteries adds more to the cost relative to the capacity of the battery. As a result, they have mainly been used in large installations for utility load levelling and are not used in other applications (Fig. 3).

4.2.3. Sodium-Nickel chloride

Na-NiCl₂ batteries also use a beta-alumina electrolyte but instead of a sulfur electrode the cathode is nickel chloride dissolved in sodium aluminium chloride (NaAlCl₄) as a molten salt which conducts sodium ions [47]. On discharge sodium reacts





2Na + xS ≓ Na₂ S_x

Fig. 3. Chemistry and principal components of a sodium-sulfur battery.

with nickel chloride to form nickel metal and sodium chloride. The system operates at a somewhat lower temperature than

Na-S batteries at \sim 300 °C but nonetheless needs heating, insulation and thermal management. Energy density is high but lower than Na-S batteries and a long cycle life is achieved. There are demonstrator batteries installed for utility energy storage and limited deployment in other applications (Fig. 4).

4.2.4. Nickel-cadmium

Ni-Cd batteries are widely used for industrial applications because they are very robust under conditions of mechanical and electrical abuse [48–50]. They have been used for utility energy storage but they are relatively expensive. There are two main types of construction with pocket plates of plated steel containing the active materials or sintered Ni electrodes impregnated with the active materials. Higher performance is achieved with sintered electrodes. Nickel-metal hydride (Ni-MH) batteries offer superior performance to Ni-Cd batteries but with a substantial cost premium and they are not used for BESS (Figs. 5 and 6).

4.2.5. Flow batteries

For utility energy storage flow batteries have some potential. There are various chemistries but they all have energy producing cells with remote storage of active materials and so batteries with very large capacities are possible [48,51–53]. Vanadium redox batteries (VRB) have cells with carbon felt electrodes which have an aqueous acidic vanadium sulfate solution pumped through with





$Cd + 2NiOOH + 2H_2O \Rightarrow Cd(OH)_2 + 2Ni(OH)_2$

Fig. 5. Chemistry and principal components of a nickel-cadmium battery.







different valence states separated by an ion selective membrane (Fig. 7). At the positive electrode V^{5+} is converted to V^{4+} and at the negative electrode V^{2+} is converted to V^{3+} on discharge. The vanadium sulfate solution is stored in tanks and in principle there is no limit to the quantity and therefore the capacity of the battery. On recharge the reverse reactions occur and the materials are regenerated. In practice, the batteries are complex and the materials are expensive but the claimed life is very long. To date, only a small number of demonstrator systems have been installed



2Na + NiCl₂ ≓ Ni + 2NaCl

Fig. 4. Chemistry and principal components of a sodium-nickel chloride battery.

 $VO_2^{+} + V^{2+} + 2H^{+} \rightleftharpoons VO^{2+} + V^{3+} + H_2O$

Fig. 7. Chemistry and principal components of a vanadium redox flow battery.



 $Zn + Br_2 \rightleftharpoons ZnBr_2$

Fig. 8. Chemistry and principal components of a zinc-bromine battery.

and VRB batteries are only suitable for utility energy storage because of the size of battery envisaged.

The zinc-bromine (Zn-Br₂) battery is another type of flow battery (Fig 8). The cell reaction is for Zn to react with Br₂ to form zinc bromide [54,55]. The Br₂ is in aqueous solution as an organic complexing agent and is pumped into the cells which have carbon electrodes and a microporous plastic separator. Metallic Zn is deposited on charge and although the Br₂ is stored in tanks, there is a limit to the capacity for any given design imposed by the Zn electrode. Costs are lower than VRB batteries but the projected life is shorter. Bromine release is a potential hazard and needs to be managed. As for other flow batteries, Zn-Br₂ batteries have only been used for utility applications in small numbers [10].

There are a number of other types of flow battery such as ironchromium but they have not been used extensively.

4.2.6. Comparison of utility energy storage systems

Table 1 (below) gives some broad indications of the installed cost, life and efficiency of various energy storage systems. For BESS, the life is given as the battery life whereas the power conversion equipment will have a life of 25 years or more with correct maintenance. Fig. 9 shows in simplified form the range of discharge durations, power and applications for various battery systems and also PHS and CAES. UPS and power quality systems require virtually immediate response but the duration will be in the range from seconds to minutes. Lead-acid batteries are ideal for this type of duty cycle and are extensively used for UPS. They are also being used for utility applications for power quality. Ultrabatteries and the Axion PbC battery are also suitable for these applications. Ni-Cd batteries are not widely used for BESS but are used to stabilise networks. Li-ion batteries may be adapted for high-rate performance but this adds cost and they are better suited to moderate rates of discharge typical of transmission service operator (TSO) and distribution service operator (DSO) reinforcement. Similarly Na-S and Na-NiCl₂ batteries are used where there

Table	1	

Comparison	of key	parameters for	or energy	storage	systems.
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are moderate rates of discharge. The performance of flow batteries and their ability to store larger quantities of liquid negative electrode and positive electrode materials moves their preferred applications further towards longer duration energy storage. They also lack the immediate response of conventional batteries as the pumps and other ancillary plant needs a short time to start up. Lead–acid batteries can cover a wide range of requirements and may be further optimised for particular applications (Fig. 10).

5. Operational experience

Lead-acid batteries have been used for energy storage in utility applications for many years but it has only been in recent years that the demand for battery energy storage has increased. It is useful to look at a small number of older installations to learn how they can be usefully deployed and a small number of more recent installations to see how battery technology has moved forward and the directions for the future.

5.1. BEWAG, Germany

The BEWAG BESS facility was installed in 1986 to provide spinning reserve and frequency regulation for the electricity network in West Berlin when it was an isolated network not interconnected with the then East Germany. The battery had a capacity of \sim 14 MWh and was comprised of 12 parallel strings each with 590 cells with a capacity of 1000 Ah. The cells were tubular flooded cells with negative grids made from lead plated expanded copper mesh and pasted in a normal manner. The increased conductivity of the negative plates in tall tubular cells leads to a more uniform current distribution between the top and bottom of the plates and better performance [56–58].

The battery ran for 9 years from installation until 1995 although in the last two years of operation, Germany had been re-united. The battery was inter-connected to the grid and the need for battery support was reduced. In the first seven years of operation, it had a capacity turnover of 7000 times the nominal capacity and there were no reported problems. The battery supported a 30 kV distribution system and the power delivered for frequency control was limited to 8.5 MW but for spinning reserve this was increased to 17 MW. The system fully satisfied the technical requirements for maintaining the stability of an island network and showed a high level of reliability.

5.2. Southern California Edison, Chino, California

Southern California Edison (SCE) installed a 10 MW, 40 MWh battery at a sub-station in Chino which became operational in 1988 [8,59]. The battery comprised of eight parallel strings of 1032 cells with a capacity of 2600 Ah. The cells were pasted plate cells with antimonial grids and used compressed air for electrolyte agitation to avoid stratification. There were systems for water addition, acid-level indicators, temperature measurement and overall battery

System	Life, years	Cycles	Energy efficiency, %	Installed system cost, \$/kWh
PHS	50	20000	80	250-350
CAES	25	10000	65	200-250
Lead-acid	15	2000	85	400-600
Ni-Cd	20	2000	85	1200-1500
Li-ion	15	2500	90	1250-1500
Na-S	10	4000	75	600-800
Na-NiCl ₂	10	4000	75	750-1000
VRB	15	10000	70	750-850
Zn-Br ₂	7	3000	70	600-800



Fig. 9. Type, power rating and discharge time for different energy storage systems.

management. The battery had a design life of 2000 cycles over an eight year period and in fact operated for nine years. The power conversion system was connected to a 12.5 kV line that in turn fed into a 69 kV line from the sub-station. Battery efficiency was measured as 81% and the power conversion efficiency was 97%.

Since this was an experimental facility, it was used to demonstrate capabilities for peak shaving, load levelling, load following, spinning reserve, transmission line support, frequency control, voltage control, VAR control and black-starts. One particular feature of the battery was its use to damp low frequency oscillations which can occur on long transmission lines. It was shown that by modulating battery power output, these fluctuations could be reduced although this was limited by the power output available. Switching from idle to full charge or discharge could be achieved in <20 ms. The project was successful in demonstrating that a large lead-acid battery could perform a wide range of duty cycles reliably over an extended period of time.

5.3. Metlakatla, Alaska

Metlakatla is a small community on an island off the coast of Alaska and its power needs are supplied by a hydroelectric generator and a diesel powered generator. The demand is variable and had high peaks because of the operation of a commercial sawmill. Before a BESS was installed, diesel generation was used for peak demand and the hydroelectric generator was not used to full capacity. This also resulted in inefficient use of the diesel generator to follow the load. An analysis of the system showed that a battery could stabilise and improve power quality by reducing voltage and frequency variations and reduce reliance on diesel generation which would result in savings in fuel costs that were high because of the remote location.

A 1.6 MW peak, 1.0 MW continuous battery was commissioned in 1997 and has operated successfully since then [60]. The battery consists of a single string of 378 2V modules each with a low rate capacity of 3600 Ah. Each module consists of three VRLA AGM 1200 Ah cells in parallel. The battery is connected through a power conversion system to a 12.5 kV distribution network. In 2000 the sawmill was closed because of environmental concerns regarding deforestation but the system continues to operate with reduced demand. The system operates in a PSoC mode using excess hydroelectric power to charge the batteries and is charged and discharged to maintain frequency and voltage within prescribed limits. Equalisation charges are required at 6-monthly intervals. A physical examination and electrical tests on cells removed after a period in service showed that they were in good condition, and was likely to exceed its design life. The level of overcharge reported after three years in operation was only 0.8% which is a strong factor in reducing the degradation of the battery.

5.4. Lerwick, Shetland Isles, Scotland

The Shetland Isles in Scotland has an electricity supply network with a 66 MW diesel generating plant and \sim 11 MW of wind power. There is some thermal storage in use and a BESS with 3 MWh of capacity and a 1 MW peak output has been installed to reduce the demand on the diesel generation and increase the proportion of wind power that can be used. The system was installed in 2013 and has operated successfully since that time providing a 20% reduction in peak demand for diesel generation with savings in fuel costs and improvements in power quality [61].

The battery comprises of 12 parallel strings of 264 cells with a nominal voltage of 528 V and a capacity of 1000 Ah. The cells are VRLA AGM types with carbon loaded negative active materials and high density positive active materials mounted horizontally in steel enclosures. The charging parameters are carefully regulated and a recharge factor of 5% is specified. Detailed monitoring of the battery is carried out both locally and remotely by the battery



Fig. 10. Lead-based Ultrabattery[®] used for frequency regulation at Lyon Station, Pennsylvania.

supplier. Thermal management is important for uniform operation of the battery. Safety systems include hydrogen detection and dispersion as well as conventional fire suppression equipment. Power conversion is through two 500 kW inverters to a transformer to an 11 kV grid connection.

The lessons learned from this installation are that current sharing between strings and recharge factor uniformity are useful parameters to identify the proper functioning of the battery and that a high level of measurement of voltage and temperatures is useful to ensure efficient maintenance activity. Heat output from the battery needs to be managed. Equalisation charges may be applied as necessary. The overall efficiency of the installation was measured as ~84%. This is a round trip efficiency based on the energy input for charging and the energy output on discharge. The recharge factor was 105%.

5.5. Lyon Station, Pennsylvania

The DSO for a large part of the Eastern part of the USA has installed a large hybrid lead battery/supercapacitor (Ultra-Battery[®]) in Lyon Station, Pennsylvania for frequency regulation (Fig. 10). This was installed in 2012 and has been shown to be highly effective in stabilising the network. There are four batteries each feeding into 900 kW inverters which in turn feed into a 13.8 kV line continuously to provide frequency regulation. Each string is comprised of 480 2 V VRLA cells. The hybrid batteries have a total of 3.6 MW of power capability and 3 MW of power can be exchanged either as output or input [62]. The system has been shown to be 92–95% DC/DC efficient and in performing regulation services has an average AC to AC efficiency of 80%. The original cells are performing well and one string has been replaced with a higher performing UltraBattery[®] variant.

5.6. King Island, Tasmania

Hydro Tasmania, an Electricity Utility in Australia has integrated a 3 MW UltraBattery [®] BESS from Ecoult at part of an island microgrid they have implemented on King Island in Bass Strait. The island grid supports the residential and commercial electricity needs of the island which has a population of around 1700 people. The BESS complements other components of the microgrid such that the system often runs for continuous periods of more than 24 h using electricity generated from renewable sources (wind and solar) alone with the BESS shifting energy from periods of excess generation to periods where extra energy is needed to match load as well as contributing to ancillary services like frequency management. The Hydro Tasmania solution has significantly reduced the amount of fossil fuel (diesel) consumed to meet the island's energy needs and the UltraBattery ® batteries in the BESS which has been operated for a number of years continue to operate very reliably. UltraBattery ® batteries have now been used in many grid and renewable integration projects and recent projects include the integration of reserve power functions and the ability to move seamlessly from grid ancillary support to full islanded microgrid modes for power continuity during times of grid failure.

5.7. Aachen, Germany

A large battery system was commissioned in Aachen in Germany in 2016 as a pilot plant to evaluate various battery technologies for energy storage applications. This has five different battery types, two lead-acid batteries and three Li-ion batteries and the intention is to compare their operation under similar conditions. Each battery is grid connected through a dedicated 630 kW inverter. The lead-acid batteries are both tubular types, one flooded with lead-plated expanded copper mesh negative

grids and the other a VRLA battery with gelled electrolyte. The flooded battery has a power capability of 1.2 MW and a capacity of 1.4 MWh and the VRLA battery a power capability of 0.8 MW and a capacity of 0.8 MWh. The Li-ion batteries are lithium-manganese dioxide, lithium iron phosphate and lithium titanate [63].

The experience from this project to date is that battery energy storage can control reactive power in a network, maintain stability and provide useful support to the network. It is intended to evaluate the economic aspects of different methods of operation as the work proceeds. It has been confirmed that batteries can be installed and put into service quickly close to consumers. The behaviour of Li-ion and lead–acid batteries is different and there are likely to be duty cycles where one technology is favoured but in a network with a variety of requirements it is likely that batteries with different technologies may be used in order to achieve the optimum balance between short and longer term storage needs.

6. Sustainability

Sustainability is important for all products and batteries are subject to strict regulation regarding collection and recycling. For lead-acid, collection is highly efficient with high recycling rates in full compliance with all environmental and other legislation [65]. The recycling industry operates economically without charges to users and provides a net credit at end-of-life. For Li-ion batteries, there are collection and recycling operations in place but they are not economic and there is a charge for reprocessing which is not offset by the value of recovered materials. For Ni-Cd and Ni-MH batteries there are collection and reprocessing systems in operation but Ni-Cd is little used for energy storage and Ni-MH not at all. Other chemistries including Na-S, Na-NiCl₂ and the various flow batteries have no recycling infrastructure in place. In view of the position of Li-ion batteries in this sector, the recycling and sustainability of Li-ion batteries will be considered in more detail [64].

6.1. Lead-acid battery recycling

Lead is the most efficiently recycled commodity metal and in the EU and USA, more than 99% of lead-based batteries are collected and recycled in a closed loop system. This is a recycling rate higher than any other mass consumer product and in Western countries 95–99% of end-of-life batteries are recycled [64]. Batteries typically contain 65% by weight of lead and most of this can be recovered. The bulk of the scrap collected is from used automotive batteries with a minor part from industrial batteries. Processes are designed to recover polypropylene case materials and but other polymers such as acrylonitrile-butadiene-styrene or styrene-acrylonitrile used in some industrial batteries are not usually recovered. If larger quantities of scrap industrial batteries are in the mix, processes to recover other polymers may become economic. For industrial batteries, brass inserts, copper connectors and alloys containing antimony may also add value to the scrap.

The recycling process starts with battery breaking which crushes batteries so that the acid is drained and collected. The batteries are then broken up into small pieces and flotation processes are used to separate polypropylene from metallic lead, battery paste and other plastics. Battery paste may be de-sulfurised using sodium carbonate and with the acid converted to sodium sulfate for external sale. The polypropylene is washed and sold for re-use. The paste and the metallic lead are then smelted with reducing agents and fluxes to produce lead bullion. This is then refined to remove impurities in sequence to produce pure lead to the required purity. This may be supplied for battery production in this form or alloyed to the customer specification. The drosses from refining are smelted to recover metals such as antimony, tin and

Table 2

Comparison of technical and other features of lead-acid and Li-ion batteries for energy storage service.

System	Lead-Acid	Li-ion
Energy Density	35–40 Wh/kg (1)	150–180 Wh/kg
	80–90 Wh/l	300–350 Wh/l
Power Density	250 W/kg (1)	800W/kg
	500 W/l	800 W/I
High Temperature Performance	to 40°C	to 50°C
Low Temperature Performance	to -30 °C	to -20 °C
Charge Acceptance	Good	Better
Cycle Life	1500-5000	1000–5000
Overall Service Life	15 years	10–15 years
Reliability	Proven	Needs to be assessed for longer times
Sustainability	Excellent	Recovery methods uneconomical
Safety	Excellent	Issues to be resolved
Cost (battery system only)	\$150-200/kWh	\$600-\$800/kWh

Note (1): Bipolar lead-acid batteries are being developed which have energy densities in the range from 55 to 60 Wh/kg (120–130 Wh/l) and power densities of up to 1100 W/kg (2000 W/l).

copper. Silver may also be recovered. The process is highly developed and high efficiencies are achieved.

In terms of value, for every tonne of scrap batteries, \sim 650 kg of lead is recovered. Polypropylene and sodium sulfate will add additional value but this has to be offset with the processing costs. An end-of-life credit will be provided for lead batteries with battery recycling carried out in full compliance with environmental regulations.

6.2. Li-ion battery recycling

At present the bulk of Li-ion batteries being recycled are small consumer cells with cobalt oxide cathodes. There are very few other types being collected and virtually no EV, HEV, industrial or energy storage cells at end-of-life so the recycling operations are designed for today's scrap batteries. The packing and transport regulations for Li-ion batteries are very stringent which adds costs and if Li-ion batteries are damaged, the requirements become very onerous. Energy storage batteries will need to be disassembled to separate cells from connectors, cooling systems, module components and other components. The costs of processing depend on the nature of the scrap and whether it is contaminated with other materials. There is a risk that Li-ion batteries will end up in landfill if the regulations are not strictly enforced.

The business model adopted by recyclers is to charge a processing fee and if there are materials of value there is a credit. There are pyrometallurgical and hydrometallurgical processes in operation, some dedicated to Li-ion batteries, others processing mixed scrap. Pyrometallurgical processes followed by hydrometallurgical processing allow Co, Ni and Cu to be recovered but only Co has any significant value. Newer chemistries such as NCA and NCM contain much less Co and LFP cells have no material of value to recover. Overall there will be a net disposal cost for Li-ion batteries at end-of-life [64].

6.3. Life cycle energy comparisons

In terms of sustainability, it is important to look at the total amount of energy used in the manufacture of products. This may be estimated as a cradle-to-factory gate figure to provide a measure of the difference between battery chemistries. For lead-acid batteries the energy used is 30 MJ/kg or 0.6 MJ/Wh and for Li-ion batteries, 170 MJ/kg or 1.7 MJ/Wh [64]. This is a large difference and needs to be carefully considered when looking at the overall impact of an investment on the environment. Similar differences are evident for the greenhouse gas emissions (CO₂) in that the quantity released in lead–acid batteries. For volatile organic

compounds (VOC), carbon monoxide (CO), nitrogen oxides (NO_x) , particulate matter (PM) and sulfur oxides (SO_x) , emissions for Liion battery production are in all cases higher than for lead-acid battery production.

7. Concluding remarks

This paper provides an overview of the performance of lead batteries in energy storage applications and highlights how they have been adapted for this application in recent developments. The competitive position between lead batteries and other types of battery indicates that lead batteries are competitive in technical performance in static installations. Table 2 provides a summary of the key parameters for lead-acid and Li-ion batteries. Lead batteries cover a range of different types of battery which may be flooded and require maintenance watering or valve-regulated batteries and only require inspection. For many energy storage applications with intermittent charging input and output requirements, especially with solar PV input, batteries are not routinely returned to a fully charged condition and where the battery is required to absorb power as well as deliver power to the network, PSoC operation becomes the normal mode. There have been substantial improvements in lead-acid batteries in this area especially with the use of carbon additives to the negative plate but this continues to be an area of active development and further improvements in performance should be achieved. There are also other types of lead batteries, particularly batteries with a hybrid construction with supercapacitor elements combined with a conventional negative plate. These offer further improvements in shallow cycle performance. Safety needs to be considered for all energy storage installations. Lead batteries provide a safe system with an aqueous electrolyte and active materials that are not flammable. In a fire, the battery cases will burn but the risk of this is low, especially if flame retardant materials are specified. Li-ion batteries have a much higher energy density, highly reactive component materials and a flammable electrolyte. Safety engineering needs to be to a very high standard to ensure the risk of thermal runaway, fire and explosion is managed. Other battery systems also have safety issues that need to be controlled. An issue with all battery technologies is sustainability. There are strict regulations regarding collection and recycling of all types of battery and mandated efficiency targets irrespective of the broader societal needs to ensure that all goods form part of a circular economy. For lead batteries, there is an established recycling infrastructure in place that operates economically in full compliance with all environmental regulations. For Li-ion and other chemistries used for battery energy storage, recycling processes do not recover significant value and will need to be substantially

improved to meet current and future requirements. Lead batteries have a long history of use in utility energy storage and their capabilities and limitations have been carefully researched. Their reliability is well established and they can be adapted for a wide range of duty cycles within this sector which will continue to ensure they provide a good solution that is competitive to other approaches.

References

- [1] O. Palizban, K. Kauhaniemi, J. Energy Storage 6 (2016) 248–259.
- [2] X. Luo, I. Wang, M. Dooner, Appl. Energy 137 (2015) 511–536.
- [3] X. Tan, Q. Li, H. Wang, J. Electr. Power Energy Syst. 44 (2013) 179-191. [4] H. Chen, T.N. Cong, W. Yang, C. Tan, Y. Li, Y. Ding, Prog. Nat. Sci. 19 (2009) 291-
- 312 [5] H. Ibrahim, A. Ilinca, J. Perron, Renew. Sust. Energy Rev. 12 (2008) 1221-1250.
- [6] P.J. Hall, E.J. Bain, Energy Policy 36 (2008) 4352-4355.
- [7] C. Pillot, The rechargeable battery market and main trends 2014-2025, 15th European Lead Battery Conference, Valletta Malta, 2016.
- [8] C.D. Parker, J. Garche, in: D.A.J. Rand, P.T. Moseley, J. Garche, C.D. Parker (Eds.), Battery Energy Storage Systems for Power Supply Networks, in Valve-Regulated Lead-Acid Batteries, Elsevier, 2004, pp. 295–326. [9] D.A.J. Rand, P.T. Moseley, in: P.T. Moseley, J. Garche (Eds.), Energy Storage with
- Lead-Acid Batteries, in Electrochemical Energy Storage for Renewable Sources and Grid Balancing, Elsevier, 2015, pp. 201-222.
- [10] D. Pavlov, Lead-Acid Batteries: Science and Technology, Elsevier, 2011.
- [11] P.T. Moseley, D.A.J. Rand, K. Peters, J. Power Sources 295 (2015) 268-274.
- A. Jaiswal, S.C. Chalasani, J. Energy Storage 1 (2015) 15–21.
 W.-L. Zhang, J. Yin, Z.-Q. Lin, J. Shi, C. Wang, D.-B. Liu, Y. Wang, J.-P. Bao, H.-B. Lin, J. Power Sources 342 (2017) 183-191.
- [14] www.fireflyenergy.com.
- [15] J. Lannelongue, M. Cugnet, N. Guillet, A. Kirchev, J. Power Sources, 352 (2017) 194-207
- [16] S. Christie, Y.S. Wong, G. Titelman and J.Abrahamson, US Patent 9 543 589, 10 January 2017
- [17] Y.M. Volfkovich, T.M. Serdyuk, Russ. J. Electrochem 38 (2002) 935. [18] E. Buiel, E. Dickinson, A. Stoermer, S. Schaeck, Dynamic charge acceptance of lead-Acid batteries in microhybrid board net, 12th European Lead Battery Conference, Istanbul, 2010.
- [19] www.axionpower.com.
- L.T. Lam, N.P., Haigh, C.G. Phyland and D.A.J. Rand, US Patent 8 232 006, 31 July [20] 2012
- [21] A. Cooper, J. Furukawa, L.T. Lam, M. Kellaway, J. Power Sources 188 (2009) 58.
- [22] T.J. Partington, US Patent, 7 541 113, 2 June 2009.
- [23] P.G. Borden, US Patent Application, 2017/0200980, 13 July 2017.
- [24] www.gridtential.com.
- [25] www.electriplast.com.
- [26] E.O. Shaffer II and W.B. Brecht, US Patent 8 357 409, 22 January 2013.
- E.O. Shaffer I.I., Advancing the energy power envelope of lead-Acid batteries [27] with bipolar design, 15th European Lead Battery Conference, Valletta Malta, 2016.
- [28] G.J. May, Secondary batteries -Lead-Acid systems: performance, in: J. Garche, C. Dyer, P.T. Moseley, Z. Ogumi, D.A.J. Rand, B. Scrosati (Eds.), Encyclopaedia of Electrochemical Power Sources, 52009, pp. 693-704.
- [29] G.J. May, Secondary batteries -Lead-Acid systems: stationary batteries, in: J. Garche, C. Dyer, P.T. Moseley, Z. Ogumi, D.A.J. Rand, B. Scrosati (Eds.), Encyclopaedia of Electrochemical Power Sources, 42009, pp. 859-874.

- [30] 3 March, Energy Storage Packing Some Power, The Economist (2012).
- [31] F.C. Figueiredo, F.C. Flynn, IEEE Trans. Energy Convers. 26 (2006) 804-809.
- [32] T.Fujihara. H. Imano, K. Oshima, Hitachi Rev. 47 (1998) 199-202. [33] W.F. Pickard, Proc I.E.E.E. 100 (2012) 473-483.
- [34] S.V. Papaefthymiou, P.G. Karamanou, S.A. Papathanassiou, M.P. Papadopoulos, I.E.E.E Trans Sust Energy 1 (2010) 163-172.
- [35] R. Madlener, J. Latz, Appl. Energ. 101 (2013) 299-309.
- [36] M. Raju, S. Kumar Khaitan, Appl. Energ. 89 (2012) 474-481.
- [37] N. Hartmann, O. Vohringer, C. Kruck, L. Etrop, Appl. Energ. 93 (2012) 541–548. [38] R. Pena-Alzola, R. Sebastian, J. Queseda, A. Colmenar, I.E.E.E Int Conf Power Eng Energy Electr Drives (2011) 1-6.
- [39] F. Diaz-Gonzalez, A. Sumper, O. Gomez-Bellmunt, F.D. Bianchi, Appl. Energ. 110 (2013) 207-219.
- [40] R. Sebastian, R. Pena-Alzola, Renew. Sust. Energy Rev. 16 (2012) 6803-6813.
- [41] P. Kurzweil, K. Brandt, Overview lithium rechargeable systems, in: J. Garche, C. Dyer, P.T. Moseley, Z. Ogumi, D.A.J. Rand, B. Scrosati (Eds.), Encyclopaedia of Electrochemical Power Sources, 52009, pp. 1-26.
- [42] D. Linden, T.B. Reddy (Eds.), Handbook of Batteries, McGraw-Hill, New York, 2011.
- [43] C. Daniel, J.O. Besenard (Eds.), Handbook of Battery Materials, Wiley-VCH, Weinheim, 2011.
- [44] D.A.J.P.T. Rand Moseley, in: P.T. Moseley, J. Garche (Eds.), High Temperature Sodium Batteries for Energy Storage, Elsevier, 2015, pp. 201–222.
- [45] N. Kawakami, Y. Iijima, M. Fukuhara, M. Bando, Y. Sakanaka, K. Ogawa, I.E.E.E Int Symp Ind Electron (2010) 2371-2376.
- [46] S. Tewari, N. Mohan, IEEE Trans. Power Syst. 28 (2011) 532-541.
- [47] C.-H. Dustmann, J. Power Sources 127 (2004) 85-92.
- [48] K.C. Divya, J. Oostergaard, Electr. Power Syst. Res. 79 (2009) 511-520.
- [49] A. Poullikkas, Renew. Sust. Energy Rev. 27 (2013) 778-788.
- [50] M.A. Fetchenko, S.R. Oshinsky, B. Reichmann, K. Young, C. Fierro, J. Koch, J. Power Sources 165 (2007) 544-551.
- [51] J.P. Barton, D.G. Infield, IEEE Trans. Energy Convers. 19 (2004) 441-448.
- [52] P. Leung, X. Li, C. Ponce de Leon, L. Berlouis, C.T.J. Low, F.C. Walsh, RSC Adv. 2 (2012) 101-125.
- [53] L.F. Arenas-Martinez, C. Ponce de Leon, F.C. Walsh, J. Energy Storage 11 (2017) 119-153.
- [54] T. Nguyen, R.F. Savinell, Electrochem. Soc. Interface 19 (2010) 54-56.
- [55] T.K.A. Brekken, A. Yokochi, Z.Z. Yen, H.M. Hapke, D.A. Halamay, IEEE Trans. Sust Energy 2 (2010) 69-77.
- [56] R. Kiessling, J. Power Sources 19 (1987) 147–150.
 [57] R. Wagner, M. Schroeder, T. Stephanblome, E. Handschin, J. Power Sources 78 (1999) 156-163.
- [58] R. Wagner, J. Power Sources 67 (1997) 163-172. December, Chino Battery Energy Storage Power Plant: EPRI TR101787, Final [59]
- Report Project RP 2870-03 (1992).
- [60] J. Szymborski, G.W. Hunt, R. Jungst, Electric energy storage applications 2000 (EESAT 2000), IEEE Power Eng. Soc. (2000).
- [61] P. Stevenson, Operational experience of a 3 MWh VRLA energy storage system, 15th European Lead Battery Conference, Valletta Malta, 2016.
- [62] Ecoult, White Paper, Public-Domain Test Data Showing Key Benefits and Applications of the UltraBattery [®] (January 2014, www.ecoult.com).
- [63] C. Folke, M5BAT project, 15th European Lead Battery Conference, Valletta Malta, 2016.
- [64] J.L. Sullivan, L. Gaines, A review of battery life cycle analysis: state of knowledge and critical needs, Argonne Nat, Lab. (2010) (ANL/ESD/10-7).
- [65] A.J. Davidson, J. Binks, J. Life Cycle Assess. 21 (2016) 1624-1636.