

Grid-Connected Aqueous based Batteries: Status and Research Assessment

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1. Introduction: Generic Properties of Aqueous Batteries

Batteries based on aqueous electrolytes have a number of advantages over their non-aqueous counterparts that make them attractive for grid-connected energy storage. However, they also have a number of disadvantages that must be taken into consideration, and which present research opportunities. The much discussed issue of gravimetric energy density (kW kg^{-1}) is not especially relevant because grid-connected batteries are generally not required to be portable.

In general, aqueous batteries have the advantage of ease of manufacture (no need for a controlled inert atmosphere). Related to this, they have lower costs than their high temperature and non-aqueous equivalents. However, they were not specifically designed for grid connection and research is needed to either redesign them or to develop new aqueous based chemistries. Their principal disadvantage is that they have lower cell operating voltages (1.2 V for Ni-Cd, 2 V for Lead-Acid). This means that more cells need to be connected in series to achieve the overall operating voltage for connection to an inverter and step-up transformer, typically 600V.

The aqueous electrolyte generally gives them favourable safety features, especially with regard to flammability and thermal runaway during charge/discharge. Other important characteristics such as efficiency, lifetime, power to energy ratio (MW/MWh) and use of scarce materials vary considerably and are considered on a case-by-case basis.

At present, lead acid cells are the most common aqueous-based battery system and account for the majority of battery sales worldwide. It was reported that during 2010 the use of lead acid batteries in China achieved a 75% connection rate to all new photovoltaic systems; likewise, during 2008, lead acid technology held 79% of the US rechargeable battery market share.

Here, we consider a number of promising aqueous based batteries and assess them for development as grid storage devices. Each section is devoted to a different class of aqueous battery, which outlines their general characteristics, gives the basic operating chemistry with the following convention:

1. Negative electrode (anode) discharge reaction left to right as written
2. Positive electrode (cathode) discharge reaction left to right as written

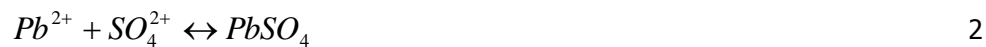
An assessment of either current deployment or grid connection potential is then given. Here we are assessing the possibility of creating a target battery of $\sim 1\text{MW}/1\text{MWh}$ battery capable with a ~ 10 year life cycle (~ 5000 charge/discharge cycles). Finally, we outline the research priorities needed for aqueous batteries as a whole.

2 Lead acid batteries

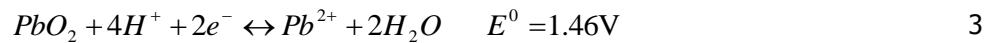
General Characteristics: The oldest example of a practical rechargeable battery was developed by Gaston Planté using lead and sulphuric acid in 1859. This technology dominates the global market for small-medium scale electrochemical energy storage applications. They are widely used in automotive applications for engine starting, lightning and ignition.

In their simplest form, lead acid batteries consist of a metallic lead as negative electrode, lead dioxide as positive electrode and a dilute solution of sulphuric acid electrolyte.

Battery chemistry: During the discharge, the metallic lead (negative) electrode is oxidized to Pb^{2+} which precipitates as $PbSO_4$:



During discharge, the positive lead oxide (PbO_2) electrode is reduced to Pb^{2+} and subsequently a $PbSO_4$ precipitate:



The most common problem in the lead acid battery is the negative electrode sulphation, which is the formation of nearly insoluble crystals of lead sulphate. During charging these crystals regenerate to a minimal extent, adversely affecting cell efficiency and lifetime.

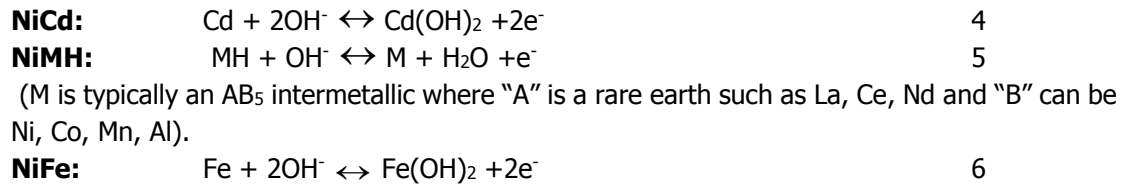
Critique for Grid Connection: Lead acid batteries have been used as stationary storage devices in electrical grid in places as California (10MW/40MWh), Hawaii (15 MW/3.75 MWh), Puerto Rico (20 MW/14 MWh), Germany (8.5 MW/8.5 MWh), among others places. Since the lead acid battery presents 2.1 V of operating voltage and 40Ah of capacity, it is necessary to use 285 cells in series to obtain a system with approximately 600 V and 42 cells in parallel to obtain 1 MWh, resulting in a system with 11970 cells (a car battery has 6 cells in series with 12.6 V operating voltage and 504 Wh).

Lead acid batteries have typical self-discharge rates of 4-20% per month, cycle efficiency ~63-90%, low cost materials and they can be easily recycled after use. However, the low cycle life (~1000) and high maintenance costs elevate the life-cycle cost. In addition, material toxicity is a concern.

3 Nickel based batteries

General Characteristics: Nickel is used as the *positive* electrode for a variety of alkaline type batteries. In all of these cases, the active material is nickel oxy-hydroxide ($NiO.OH$), which is formed from nickel hydroxide during battery charging. There are a variety of materials used for the negative electrode which give different classes of Ni-based batteries. The most important in the market are nickel cadmium ($NiCd$), nickel metal hydride ($NiMH$) and nickel iron ($NiFe$).

Battery Chemistry: The respective *negative* electrode chemistries are:



During discharge, the general equation of the nickel (positive) electrode in alkaline media is



Critique for Grid Connection:

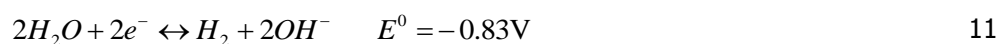
a. NiCd batteries. Research efforts in this area are centred on improving their energy density and cycle life alongside and preventing the reactions that result in self-discharge. An example of this technology being used for grid support is the system developed by GVEA that uses ~14,000 NiCd cells providing backup power of 27MW for up to 15 minutes. This system has been in operation since 2003. Not only is the toxicity of cadmium a major drawback of NiCd technologies, but also it has been recently identified that NiCd cells are associated with higher CO₂ and SO₂ emissions during their production, compared with lithium-based cells.

b. NiMH batteries: Recent improvements to cell architecture have focused on increasing the power density of NiMH cells and it remains a viable choice for use in light rail vehicles. NiMH cells are characterized by energy densities around 250-330 Whl⁻¹, a specific energy up to 100Whkg⁻¹ and they are limited to 1000 cycles. Compared to NiCd cells, they can perform roughly twice of the number of cycles but they are associated with a low energy density. Without substantial improvements, the restricted cycle life of NiMH renders them unsuitable for large-scale grid connected applications.

c. NiFe batteries: There has been renewed interest in iron-based electrodes and NiFe cells are well known for their long cycle life. They were successfully commercialised in the early 20th century fell out of favour with the advent of cheaper lead acid cells and subsequently received little attention with regards to development. This technology could provide a cost effective solution for large-scale energy storage applications due to its relative environmental friendliness, longevity, and tolerance to electrical abuse (*i.e.* cells can recover from over charge/discharge or relatively long idle periods).

The relative abundance of the raw materials required to produce NiFe cells is another aspect favouring its use. Nickel and iron are among the most abundant elements in the Earth's crust, and less abundant elements included in the cell (such as bismuth) are used in relatively small proportions, therefore NiFe cells have the potential to be manufactured at relatively low cost.

During charging water can be decomposed yielding hydrogen, a process that reduces cell efficiency. The following equation explains this process:



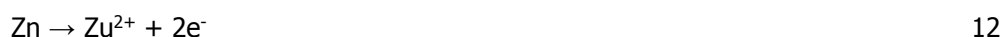
Mitigation of hydrogen production has been traditionally achieved by modification of the iron electrode formulation using the addition of components (such as sulphur or bismuth) that increase the activation energy for water decomposition. NiFe cells use strongly alkaline solutions of potassium and lithium hydroxide and selected additives (such as potassium sulphide) to prevent electrolyte decomposition.

As discussed above, a major challenge facing NiFe batteries is the evolution of hydrogen, which results in low charge/discharge efficiencies (*ca.* 50-60%) and low specific power.

4. Copper-Zinc

General Characteristics: Invented by John Frederic Daniell in 1836, the CuZn battery operates at a net cell potential of 1.08 V; and is powered by the transfer of electrons from zinc atoms to copper ions. It consists of two metal plates, each in its own container of salt soluble ion connected through a salt bridge or semi-permeable membrane. Industrially, membranes are preferred to reduce cell resistance. Cumulus Energy Storage is undertaking the commercial development of a rechargeable copper-zinc battery.

Battery Chemistry: The negative electrode, the anode, is composed of metallic zinc, in an aqueous solution of zinc sulphate. During cell discharge, the elemental zinc is oxidized to Zn(II):



Likewise, the positive electrode is metallic copper in an aqueous solution of copper sulphate. During cell discharge, the Cu(II) is reduced to metallic copper Cu(0):



Critique for Grid Connection: The presence of the salt bridge, semi-permeable membrane or ceramic spacer in this battery implies the cell had a relatively high internal resistance and therefore a portion of its energy would be consumed internally rather than being available for external work.

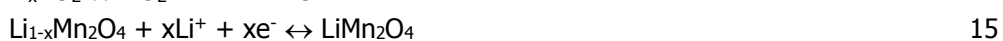
The relatively large internal resistance, and therefore I^2R losses, means that only a moderate current can be taken from these batteries. Deposition of copper in places other than the copper electrode is a problem that renders the battery inactive. In addition, when the battery is not in action, copper ions diffuse through the membrane to reach the zinc side of the battery. Copper is then deposited on the zinc plate as black cupric oxide (CuO) impairing the performance of the battery; this process is usually minimised by taking down the battery when not in use. Notwithstanding these difficulties, the CuZn battery this is a simple, safe and cost effective device with potentially important grid applications.

As mentioned, Cumulus Energy Storage is undertaking the commercial development of a rechargeable copper-zinc battery. This project aims to create safe, low cost battery systems with capacities in the region of 1MWh to 100MWh.

5. Aqueous Electrode Insertion, 'Rocking-chair', batteries

General Characteristics: 'Rocking-chair' batteries are the aqueous analogue of common insertion electrode-based Li-ion batteries. The positive and the negative materials are usually host-layered structures to facilitate the intercalation of the lithium ions. During charge and discharge lithium ions diffuse back and forth between the electrodes through the electrolyte with the corresponding flow of electrons in the external circuit. Dahn's group developed the first aqueous Li-ion battery in 1994 with a VO₂ as negative electrode and the spinel LiMn₂O₄ as positive electrode with a 5M LiNO₃ electrolyte. Other research groups have subsequently used different materials very similar to non-aqueous Li-ion technology. The company Aquion Energy have commercialized this concept based around the lowest cost materials available to them.

Battery Chemistry: Typical electrochemical reactions are:



Critique for Grid Connection: Aqueous intercalated batteries employed environmentally friendly materials, they also no have memory effect. However, the complexity of the electrochemical and chemical reactions during the insertion/de-insertion processes in aqueous systems makes them very challenging compared to organic-based batteries. A clear limitation in these batteries is the restricted stability of the stable voltage window of aqueous electrolytes. The decomposition of electrolyte occurs at 1.23 V and involves H₂ or O₂ gas evolution. This potential defines the stable operating voltage window in aqueous systems, although it is very low compared with that of the organic-based systems (3.0 V for Li-ion batteries) indicating a lower energy density storage (75 Wh/kg) but larger than Ni-Cd batteries (25 Wh/kg). There are many side reactions that limit their performance and their long cycling life. The main drawbacks of this technology are (1) the reaction of molecular hydrogen or oxygen with electrolyte decomposition, (2) proton (H⁺) co-intercalation into the host electrode, (3) reactions between electrode material and water or residual molecular oxygen, and (4) the dissolutions of electrode materials. Nevertheless, different approaches have been used to overcome these issues and commercial systems are already in the market.

Aquion Energy uses a cubic spinel LiMn₂O₄ as the positive electrode and activated carbon/NaTi₂(PO₄)₃ composite as a negative electrode. Their devices are able to work for thousands of cycles without significant capacity loss. Their smallest product (Aquion S-Line Battery Stack) with eight batteries in series have a nominal energy of 2.4 kWh at 20 hour discharge at 30°C with a round trip of efficiency ~85%. The discharge curve appears more similar to that of a supercapacitor than a conventional battery and loss of voltage with discharge poses problems in interfacing with power electronics.

6. Metal-air batteries

General Characteristics: In order to achieve greater energy densities, aqueous-based battery systems that use cell architectures more akin to that seen in fuel cells are being developed. The negative electrode consists of a metal and the positive electrode allows interaction between the metal ions and atmospheric oxygen. The challenge is to produce rechargeable (or secondary) batteries.

Battery Chemistry: Taking lithium as an example, the electrode reactions are:



Critique for Grid Connection:

a. Lithium Air: The reaction below has a potential of 2.96V and a theoretical energy density of 3460 Wh kg⁻¹:



A great deal of recent research has focused on the development of non-aqueous cells utilising metallic lithium. The introduction of a protective LISICON layer enables the utilisation of metallic lithium with aqueous electrolytes - the conversion to lithium hydroxide monohydrate has a theoretical energy density of 1910 Wh kg⁻¹ at 3.0V. However, these systems are currently in the research stage and are unlikely to be deployed at the grid scale in the near future.

b. Zinc Air: Primary zinc-air cells are a fairly mature technology that has found commercial applications in medical and telecommunications. As with other metal-air cells, a major driver for development is their high theoretical energy density (1086 Wh kg⁻¹ including oxygen). The compatibility of zinc with an aqueous alkaline electrolyte allows for substantially reduced manufacturing costs in comparison with non-aqueous based cells. However, the development of electrically rechargeable zinc-air cells has been hindered by the propensity of zinc to form dendrites upon repeated charge-discharge cycling and their low output power. A further drawback of aqueous alkaline electrolytes is that carbon dioxide is absorbed by the solution and produces insoluble, electrode blocking compounds that reduce electrolyte conductivity and impede cell performance. As a consequence, the process of air purification needs to be considered alongside cell design.

Improvements in performance require the identification of suitable robust catalysts and electrolyte additives to prevent dendrite growth. Zinc-air cells have been proposed as a suitable alternative to lithium-ion for use in electric vehicles and were successfully demonstrated by "Electric Fuel" in 2004. Currently, Eos Energy Storage is in the process of commercialising systems that use a hybrid zinc electrode and neutral pH aqueous electrolyte that avoids several of the problems historically encountered in zinc-air chemistry. Alongside a 70kWh pack designed for EVs, they are developing a grid scale (1MW, 6MWh) system that has a round-trip efficiency of 75% and is projected to last for 10,000 charge/discharge cycles. The power to energy ratio is perhaps indicative of the reduced power handling of this battery class.

c. Iron Air: An alternative cell chemistry that has received attention of late is the iron-air cell that also operates in an aqueous alkaline electrolyte. Iron-air cells do not exhibit the same stripping/redeposition problem as seen in zinc-air cells but have a lower theoretical energy density of 764 Wh kg⁻¹ and electrically rechargeable cells exhibit relatively low energy efficiencies (ca.35%). As with zinc-air cells the development of more efficient oxygen electrodes is required.

7. Research needs

Research into virtually aspect of aqueous battery technology is essential and although there are some important commercial developments, research is not as developed as for non-aqueous Li-ion. This may be because conventional Li-ion batteries are unrivalled for transport applications because of gravimetric energy density and there is an international impetus to decarbonise transport. However, this does not automatically that this battery class is best suited for grid connection: Aqueous technology is potentially the cheapest form of electrochemical storage and with clear safety advantages.

A glance at the US DoE Global Energy Storage Database:

<http://www.energystorageexchange.org/>

shows relatively few non-aqueous battery demonstration projects and it is therefore difficult to assess their true potential. Much more data is needed in this aspect.

In research terms, many aqueous based battery technologies are regarded as being "mature" technology e.g. Pb acid, NiCd and NiMH. Recent progress has only been incremental and may be better performed in an industrial context. However, innovation is still possible. In order to improve lead acid battery performance, the use of carbon in combination with Pb, or even a carbon-only electrode, has been proposed as negative electrode. This kind of modification increases the energy output and reduces the sulphation issue, increasing the cycle life to ~3000. New materials for electrode grid must also be considered. It should always be remembered that the use of Pb acid in grid applications is already well-established and is quite commonly the default battery for supporting renewables such as PV due to cost, safety and availability.

Short to medium-term battery developments (deployment 1-10 years) should concentrate on relatively simple battery structures such as NiFe and CuZn, which were not designed for grid connection but which could be easily designed to fulfil this role. Both have the advantage of utilising relatively cheap, safe and easily recyclable materials.

Due to their extended cycle life (~1000s), lower toxicity and lack of memory effects, NiFe cells are the most promising of all Ni-based technologies for large scale energy storage. As explained, the improvement of these batteries hinge on increasing their round-trip efficiency by suppressing electrolyte decomposition. Finally, the low power density of these batteries can be increased by improving the kinetic characteristics of the inter-conversion of Fe(0) to Fe(II) that takes place during the charge and discharge of the battery. There is already interesting research in this area, in particular using FeS and a variety of other electrode and electrolyte additions. It is surprising that no serious attempts have been made to apply the techniques of nano engineering to improve the power handling of this battery. Also, a survey of the literature shows little fundamental understanding of the chemical effects of additives. The Ni electrode may be regarded as a mature technology since it has been commercialised and industrially optimised over a period of decades for use in NiCd and NiMH batteries. NiFe is a highly promising technology scalable from domestic to grid that needs a collaborative electrochemistry and engineering approach. Even if the power handling cannot be improved, it is easy to conceive that their low cost and long life properties will make them ideal hybrids with other technologies for grid applications such as Lithium Titanate batteries.

CuZn batteries need significant improvements in membrane technology in terms of reduced thickness and selectivity to make it into a genuinely secondary battery. Unless this problem is solved then maintenance costs may be problematic to a highly promising technology. This would entail periodic draining of the electrolyte, purification and perhaps membrane replacement. Again, these batteries have received little attention at the fundamental level to date with very few papers appearing in the scientific literature. As with any battery, development costs are likely to be very high and need the backing of large industry to develop and deploy new separators.

Finally, in the long term (>10 years), the "rocking-chair" battery class offers a completely new battery class, one that could even make contemporary Li-ion batteries redundant, even for automotive applications. New and novel combinations of electrodes, coatings and separators need to be explored. The Aquion Energy company philosophy of starting research from economics is interesting, but this has delivered a battery that still needs considerable improvement.

The ideal aqueous battery would be one that had the longevity of NiFe, the power and cost of Aquion Energy combined with the energy density of non-aqueous rocking chair batteries. Developmentally daunting, but a worthwhile project requiring Manhattan Project-scale investments.