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Aqueous batteries as grid scale energy storage solutions

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ABSTRACT

Energy storage technologies are required to make full use of renewable energy sources, and electro-chemical cells offer a great deal flexibility in the design of energy systems. For large scale electrochemical storage to be viable, the materials employed and device production methods need to be low cost, devices should be long lasting and safety during operation is of utmost importance. Energy and power densities are of lesser concern. For these reasons, battery chemistries that make use of aqueous electrolytes are favorable candidates where large quantities of energy need to be stored. Herein we describe several different aqueous based battery chemistries and identify some of the research challenges currently hindering their wider adoption. Lead acid batteries represent a mature technology that currently dom-inates the battery market, however there remain challenges that may prevent their future use at the large scale. Nickel–iron batteries have received a resurgence of interest of late and are known for their long cycle lives and robust nature however improvements in efficiency are needed in order to make them competitive. Other technologies that use aqueous electrolytes and have the potential to be useful in future large-scale applications are briefly introduced. Recent investigations in to the design of nickel–iron cells are reported with it being shown that electrolyte decomposition can be virtually eliminated by employing relatively large concentrations of iron sulfide in the electrode mixture, however this is at the expense of capacity and cycle life.

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1. Introduction

Due to climate change and the depletion of fossil fuel reserves, governments have started to re-evaluate global energy policy. Therefore, we are experiencing an increasing demand of energy from renewable sources such as solar and wind power [1–3] and the majority of countries face challenges in the integration of an increasing share of energy coming from these intermittent sources [4–13]. Renewable sources (such as solar, wind power, etc.) are changing the energy market and they may displace significant amounts of energy that are currently produced by conventional means; this is, for example, an staggering 57% of the total demand of electricity in Denmark by 2025 [1], around 15% of the total UK energy demand by 2015 and almost 16% of China by 2020 [2]. Energy storage technologies are required to facilitate the move towards the supply of low carbon electricity [14], and are particularly useful when exploiting intermittent energy sources. Incorporating energy storage has been shown to be beneficial to various sectors of the electricity industry, including generation, transmission and distribution, while also providing services to support balancing and manage network utilization [15,16].

In large-scale energy storage systems operational safety is of prime importance and characteristics such as energy ($Wh\,l^{-1}$) and power density ($W\,l^{-1}$), which are major drivers in the development of devices for mobile applications, are of lesser concern. Other desirable characteristics for large scale energy storage systems are a low installed cost, long operating life, high energy efficiency and that they can be easily scaled from several kWh to hundreds of MWh. Different battery chemistries demonstrated for use at this scale include lead-acid, lithium-ion and sodium-based batteries. Lithium-ion batteries exhibit very high round trip efficiencies (as high as 99%), energy densities in the range of 100–200 $Wh\,kg^{-1}$ and can typically withstand 1000 cycles before fading [17]. Sodium-based batteries (sodium–sulfur, ZEBRA) operate at temperatures in the region of 300–350 °C and are characterized by a round trip efficiency of 80%, energy densities up to 150 $Wh\,kg^{-1}$ and lifetimes in excess of 3000 cycles [17].

There have been several recent incidents where lithium-ion cells and sodium–sulfur batteries have failed which has resulted in the release of toxic materials; this aspect has raised serious safety concerns over the application of these batteries to large-scale energy storage [18–21]. Not only there are safety concerns with these chemistries, but also these technologies are associated with high costs due to the materials used, manufacturing processes and auxiliary systems required for their operation. As a result of these considerations, the inherent safety and potential low cost offered by the aqueous-based electrochemical energy storage devices discussed in the following sections reveals that they can contribute positively to large-scale energy storage applications.

At present, lead-acid cells are the most recognizable aqueous-based battery system and represent a major proportion of the global battery market. For example, it was reported that during 2010 the use of lead acid batteries in China reached a staggering 75% usage of all new photovoltaic systems [22]; likewise, during 2008, lead acid technology held 79% of the US rechargeable battery market share [23]. This paper is focused on aqueous electrolyte based electrochemical energy storage technologies suitable for large-scale applications and discusses some of the challenges faced in the development of viable systems. The list of systems discussed here in is not exhaustive, but intended to give a brief overview of the area. These technologies have the potential to be integral components in future electricity supply systems providing that substantial reductions in cost can be achieved, and that safe and reliable operation can be assured.

2. Literature review

2.1. Lead acid batteries

2.1.1. Overview

The oldest example of a practical rechargeable battery was developed by Gaston Planté using metallic lead and sulfuric acid as electrolyte in 1859 [24]. Lead acid batteries may have different arrangements (i.e. series or parallel) depending on the applications. Starting batteries are widely used in automotive applications for engine starting, lighting and ignition (SLI), where peaks in current are requested intermittently. This is achieved by using thinner electrodes and separators, resulting in lower internal resistance than that of regular lead acid batteries [25,26]. In such applications the depth of discharge is kept low to maintain device longevity. On the other hand, if the desired application requires constant discharge at relatively low rates, (as in an uninterruptible power supply (UPS) or when powering small vehicles), the deep-cycle or 'marine' battery is used. This device architecture incorporates thicker electrodes to allow for a much greater depth of discharge to be utilized [27–29].

In their simplest form, lead acid batteries consist of a positive electrode composed of lead-dioxide (PbO_2), a negative electrode composed of metallic lead (Pb), and a dilute solution of sulfuric acid electrolyte. During discharge, at the cathode, lead oxide is reduced to

Pb^{2+} as indicated by Eq. (1).

$$PbO_2 + 4H^+ + 2e^- \leftrightarrow Pb^{2+} + 2H_2O \quad E^0 = 1.46\ V \qquad (1)$$
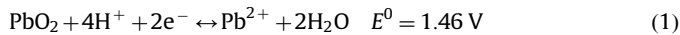
Once formed, Pb^{2+} ions precipitate in the form of $PbSO_4$, as shown in Eq. (2).

$$Pb^{2+} + SO_4^{2+} \leftrightarrow PbSO_4 \qquad (2)$$

Likewise, at the anode during discharge, metallic lead is oxidized to Pb^{2+} as presented in Eq. (3).

$$Pb \leftrightarrow Pb^{2+} + 2e^- \quad E^0 = -0.13\ V \qquad (3)$$

Finally, Pb^{2+} ions are precipitated in the form of $PbSO_4$ as indicated by Eq. (2).

Fig. 1 provides a schematic representation of a lead acid cell [24,30].

Lead acid batteries are well known for their low rate of self-discharge, complicated production process, low cost of raw materials, recyclability, and good performance over a wide range of operating temperatures. Significant developments in performance have been achieved by the introduction of a valve-regulated system and also by the addition of carbon material to the anode. The use of carbon in the Pb anode improves both cell efficiency and cycle life due to reduced $PbSO_4$ accumulation [31].

2.1.2. Negative electrodes

Most of the problems that are usually encountered with lead acid batteries are strongly dependent upon the negative electrode. Sulfation, the formation of nearly insoluble crystals of lead sulfate is, by far, the most common ageing phenomenon inherent to lead acid batteries. During charging these crystals regenerate to a minimal extent, adversely affecting cell efficiency and lifetime.

One solution to this challenge has been to incorporate a highly conductive additive (usually of carbonaceous nature) to the negative electro-active electrode to prevent sulfation while maintaining high electronic conductivity [25,26,30]. Also, it has been reported that nano-structuring the negative electrode improves electrode performance [32]. The exchange of the lead anode by a carbon electrode has also been explored. This assembly is similar to an asymmetric supercapacitor and resulted in a battery with longer cycle life [33].

Another promising design is the use of a double anode, containing a foil of metallic Pb and a second foil of carbonaceous material; such designs allow the battery to operate at high power due to supercapacitor-like behavior for an extended period in partial state of charge operation [33–35].

Although, the corrosion of the positive electrode has always been regarded as a major concern in lead-acid battery technology, the corrosion of the negative electrode has drawn an increased attention recently. The importance of corrosion control through the optimization of the electroactive materials has recently been reported [36–38].
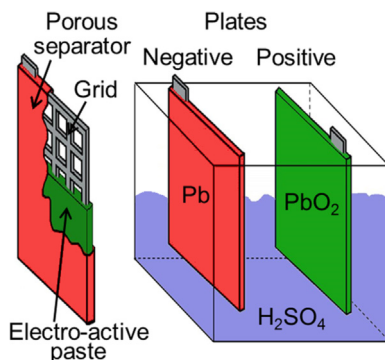

Fig. 1. Schematic representation of a lead-acid cell.

2.1.3. Positive electrodes

In order to enhance the performance of the lead-acid battery, low antimony grids are commonly used. Unfortunately, low antimony grids are prone to develop a passivation film between the grid and the electroactive material of the electrode. In addition, the corrosion of the positive electrode is well known to play a detrimental effect on the performance of the lead-acid battery. Therefore, the production of new formulations based on lead oxides [39], and different additives (conductive and non-conductive) [40], play a pivotal role in controlling corrosion and preventing passivation of positive electrodes for lead acid batteries [41]. Finally, it is important to highlight the importance of collectors for these electrodes (see Section 2.1.2).

2.1.4. Collector grids for lead acid batteries

In order to improve the energy density of lead-acid batteries development has focused on reducing the redundant weight in cells by optimizing the electrode composition and the structure of the collector grid. Improvements in the manufacture of lighter grids have been realized by electro-depositing layers of lead on highly conductive and low specific gravity substrates such as copper, aluminum, carbon, barium, indium, etc. [30,37,38,42–49].

Broadly speaking there are two main types of grid used at the positive terminal; lead–antimony and lead–calcium based grids. Unfortunately, lead–calcium grids are unsuitable for deep-discharge applications. Likewise, lead–antimony grids are associated with a reduced hydrogen overpotential, which results in considerable amounts of hydrogen being evolved during charging. It has been reported that elements such as strontium, cadmium, silver and the majority of rare earth elements can be used to produce lead–antimony or lead–calcium based alloys with enhanced performance [42,50–53]. Vitreous carbons coated with lead have also been proposed as suitable electrode grids, however due to oxygen evolution these are not well suited for use in positive plates [49,54].

2.1.5. Research challenges

Lead acid batteries are known for their low energy density, about 30 Wh kg^{-1}, which represents only 25% of the value associated with lithium-ion batteries. Other major challenges faced by this chemistry are limited cycle life, toxicity, and relatively low charge/discharge efficiency [26,42,55,56].

2.2. NiFe batteries

2.2.1. Overview

Nickel–iron batteries have been successfully developed and commercialized in the early 20th century. Nickel–iron or 'NiFe' cells are secondary batteries that fell out of favor with the advent of cheaper lead acid cells. There is renewed interest in these batteries due to their environmentally friendliness, longevity, and tolerance to electrical abuse. It is believed that this technology could provide a cost effective solution for large-scale energy storage applications, particularly where only a relatively low specific energy is required (30–50 Wh kg^{-1}).

The relative abundance of the raw materials required to produce NiFe cells is another aspect favoring their 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 [57,58]. Fig. 2 provides a schematic representation of a NiFe cell.

2.2.2. Negative electrodes

The main reaction during charging of an iron electrode under basic conditions is the reduction of ferrous ion (Fe^{2+}) to elemental iron (Fe^0). Similarly, the oxidation of elemental iron to ferrous ions, occurs during discharge of the same electrode. Eq. (4) illustrates
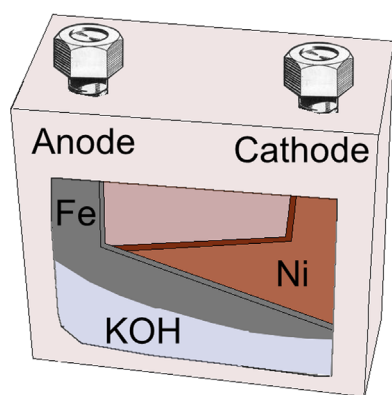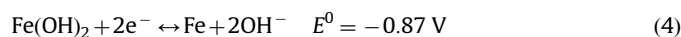
Fig. 2. Schematic representation of a NiFe cell.

the charging and discharging (forward and backward reactions respectively) processes of an iron electrode under strong alkaline conditions [59,60].

$$Fe(OH)_2 + 2e^- \leftrightarrow Fe + 2OH^- \quad E^0 = -0.87 \text{ V} \quad (4)$$

Unfortunately during charging, water can be decomposed yielding hydrogen, a process that adversely influences cell efficiency. This process of electrolyte decomposition (and therefore hydrogen evolution) accounts for a drastic reduction in the overall performance of the battery, as indicated by Eq. (5).

$$2H_2O + 2e^- \leftrightarrow H_2 + 2OH^- \quad E^0 = -0.83 \text{ V} \quad (5)$$
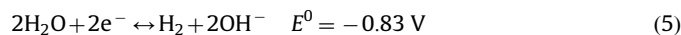
Mitigation of this process in NiFe cells has been traditionally achieved by either modification of the iron electrode formulation or by the addition of electrolyte additives (such as potassium sulfide), in such a way that the activation energy for electrolyte decomposition would be increased [61,62].

2.2.3. Positive electrodes

The positive electrode in NiFe cells is based on the nickel hydroxide/oxyhydroxide couple used in nickel–cadmium and nickel-metal hydride cells. Two polymorphs of $Ni(OH)_2$ exist, they are α-$Ni(OH)_2$ and β-$Ni(OH)_2$; they can be transformed into γ-NiOOH and β-NiOOH, respectively. However, due to the low stability of α-$Ni(OH)_2$ in alkaline media, the β-$Ni(OH)_2$ is usually used as a precursor material in alkaline batteries [63–65].

2.2.4. Electrolyte

NiFe cells use strongly alkaline solutions of potassium and lithium hydroxide and selected additives (such as potassium sulfide) to prevent electrolyte decomposition. Typically, the mitigation/prevention of hydrogen evolution during charging has been achieved by either modification of the anode or by the addition of electrolyte additives that increase the hydrogen overpotential. Other electrolyte additives such as wetting agents [66], long chain thiols [67] and organic acids [68] amongst others, have been investigated [61].

2.2.5. Research challenges

As discussed above, a major challenge facing NiFe batteries is the evolution of hydrogen, which results in low charge/discharge efficiencies (ca. 50–60%) [59,62,69], and low specific energy (30–50 Wh kg^{-1}), Another consideration with this chemistry is the toxicity of nickel which significantly influences manufacturing costs.

2.3. Aqueous 'Rocking-Chair' batteries

2.3.1. Overview

The concept of intercalation electrodes, used in lithium-ion cells, has inspired research into similar systems that replace organic solvents with aqueous-based electrolytes. This enables the use of much lower cost materials with increased ionic conductivity. Cells using intercalation electrodes are also known as 'rocking-chair' batteries [70], as ions are inserted into and removed from electrodes during charge and discharge.

2.3.2. Lithium based systems

An aqueous Li-ion cell was first reported where a VO_2 anode and $LiMn_2O_4$ spinel cathode in 5 mol l^{-1} $LiNO_3$ solution exhibited an energy density of around 75 Wh kg^{-1} [71]. This is significantly higher than that seen in lead-acid and nickel-based cells, however this system exhibited a poor cycle life [72].

A clear limitation of aqueous electrolytes is their restricted electrochemical stability as, under standard conditions, electrolysis of H_2O occurs at 1.23 V and involves H_2 or O_2 gas evolution. The energy density in aqueous-based systems has been increased by expanding the operating potential. For example, Hou et al. reported values around 342 Wh kg^{-1} at an average discharge voltage of 3.32 V when the lithium anode was covered by a polymer and LISICON film. These layers acted as a protective coating preventing the formation of lithium dendrites and to separate the lithium metal from the aqueous electrolyte [73].

To gain deeper insights into the intercalation mechanisms occurring in such cells, similar electrode materials employed in non-aqueous batteries have been considered. However an additional consideration in these systems is pH, as this influences H_2 and O_2 evolution potentials as well as the stability of the electroactive material [74].

In the case of cathode materials, which are quite stable in aqueous solutions, protons (H^+) or water molecules inserted into the host structure compete with lithium-ion insertion which reduces capacity due to obstructed transport pathways [75]. The structure of the host material is very important as each structure behaves differently throughout the insertion processes. As an example, structures such as spinel $Li_{1-x}Mn_2O_4$ and olivine $Li_{1-x}FePO_4$ cannot host H^+ meanwhile layered structures ($Li_{1-x}CoO_2$, $Li_{1-x}Ni_{1/3}Mn_{1/3}Co_{1/3}O_2$) presented a large amount of H^+ concentration in the framework in acidic media [76,77]. Moreover, dissolution of the electrode material in the electrolyte is the other limiting factor in terms of long-term cyclability. The addition of a protective surface coating onto the electrode has been shown to improve cycle life [78,79].

2.3.3. Sodium based systems

Increasing demand for lithium and its relatively low natural abundance has resulted in a search for suitable alternatives. Sodium is the most promising candidate to replace lithium as it exhibits similar chemical behavior and has a similar ionic radius (90 pm for Na^+ and 116 pm for Li^+) [80]. It has been shown that sodium can be reversibly inserted into the tunnel structure $Na_{0.44}MnO_2$ delivering a capacity of 45 mAh g^{-1} at 0.125 C [81]. It was later reported that a large format hybrid/asymmetric aqueous intercalation batteries using λ-MnO_2 as cathode materials and an active carbon in Na_2SO_4-based electrolyte could be operated over a wider range but with a lower energy density. This was further developed to replace some of the activated carbon with $NaTi_2(PO_4)_3$, and has been shown to withstand thousands of cycles without significant capacity loss. This technology has been commercialized by "Aquion Energy" who offers a range of systems from 2 kWh units for residential use to off-grid applications and grid services.

Recently, Chen et al. have shown that the use of Li^+/Na^+ mixed-ion electrolytes results in good stability [82]. In these systems, at one electrode Li^+ are exchanged between the electrolyte and electrode whereas at the other electrode Na^+ is exchanged with the concentration of Na^+/Li^+ remaining constant upon cycling.

2.3.4. Research challenges

"Rocking chair" chemistries could emerge as a potential alternative in the development of safer and higher energy density batteries in comparison with Pb-acid cells, however the secondary reactions present in all aqueous system restrict their performance and cycling life. The main challenges associated with aqueous 'rocking chair' systems have been identified as (1) electrolyte decomposition evolving H_2 and O_2 (2) side reactions with water or evolved gases (3) proton (H^+) co-intercalation into the host electrode, and (4) the dissolution of electrode materials [83].

2.4. Other technologies

2.4.1. Nickel–cadmium and Ni-metal hydride batteries

Exploiting the same reaction as the positive electrode in NiFe cells, are devices with alkaline aqueous electrolytes that use metal hydride or cadmium based negative electrodes [64]. These chemistries may be familiar, as they have been employed for many years in the consumer electronics sector, and were integral to the development of electric vehicles in the 1990s. This represents a mature battery technology that has been identified as suitable for power quality applications and grid support. Research efforts in this area are focused on improving their energy density and cycle life alongside and preventing the reactions that result in self-discharge. An example of this technology is the system developed by "GVEA" that uses almost 14,000 NiCd cells providing backup power of 27 MW for upto 15 min. This system has been in operation since 2003.

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 in the region of 250–330 Wh l^{-1}, a specific energy of upto 100 Wh kg^{-1} and are limited to around 1000 charge–discharge cycles. By comparison NiCd cells can perform roughly twice the number of cycles but are associated with a lower energy density. Not only is the toxicity of nickel and cadmium a major drawback of this technology, but it has been recently identified that NiCd cells are associated with substantially higher CO_2 and SO_2 emissions during production, when compared with lithium based cells [84].

2.4.2. Zinc air batteries

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 outstanding theoretical energy density (1086 Wh kg^{-1} including oxygen). (Another research direction that has come to prominence of late is the development of aqueous Li-air batteries which have a theoretical energy density of 1910 Wh kg^{-1} [85]).

The compatibility of zinc with an aqueous alkaline electrolyte allows for substantially reduced manufacturing costs in comparison with non-aqueous based cells. 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 [86]. A further drawback of aqueous alkaline electrolytes is that carbon dioxide can be absorbed by the solution thus producing insoluble, electrode blocking compounds that decrease electrolyte conductivity and impede cell performance. As a consequence (and similar to other metal-air systems), the process of air purification needs to be considered alongside a new engineering cell design.

Improvements in performance require the identification of suitable robust catalysts and electrolyte additives. 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" are developing a grid scale zinc-air system using a hybrid zinc electrode and a near neutral pH aqueous electrolyte.

2.4.3. Iron air batteries

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 they have a lower theoretical energy density of 764 Wh kg^{-1} compared to Zn-air batteries but higher than Pb-acid or NiFe batteries. Also the electrical rechargeable cells exhibit relatively low energy efficiencies (ca. 35%) [87]. As with zinc-air cells the development of more efficient oxygen electrodes is required.

2.4.4. Copper–zinc batteries

Another noteworthy technology utilizing aqueous electrolytes is the development of a rechargeable copper–zinc battery by "Cumulus Energy Storage". This technology is based on processes used in metal refining, this project aims create safe, low cost battery systems with capacities in the range from between 1 MWh and 100 MWh.

2.5. Summary

For large scale electrochemical storage to be viable, the materials used need to be low cost, devices should be long lasting and operational safety is of utmost importance. Energy and power densities are of lesser concern. For these reasons, battery chemistries that make use of aqueous electrolytes are favorable candidates where large quantities of energy need to be stored. Table 1 lists selected figures of merit for various aqueous battery technologies to allow for easy comparison. It is clear that certain chemistries display desirable characteristics but are hindered by poor performance in other areas.

Large scale energy storage does not demand high efficiency, nor does it require very high energy densities; the capital and operating costs of the system are more crucial design parameters. Moreover, non-aqueous batteries require the implementation of sophisticated safety systems to prevent hazardous situations (e.g. thermal runaway leading to fire). In addition, the cost and relative abundance of the reactants and raw materials required to build non-aqueous batteries remain a concern when such systems are proposed for use on the large scale. Table 2 summarizes some of the advantages and

Table 1
Figures of merit of selected aqueous batteries [17,27,31,88–91].

Technology	Cost (€ kWh^{-1})	Energy density (Wh kg^{-1})	Coulombic efficiency (%)	Life (no. of cycles)	Self-discharge (% $month^{-1}$)	Memory effect
Pb acid	25–40	30–50	50–70	300–500	30	No
NiFe	50–60	30–50	55–65	2000+	20	No
Ni–Cd	70–80	50	65–70	1500	28	Yes
NiMH	275–550	50–80	65	500–800	30	Yes
Li-ion ($LiMn_2O_4/VO_2$)	500–700	75	60	500–3000	10–	Small
Na-ion (λ-MnO_2/C)	300–400	50–60	70	–	–	–
Zn-air	5–10	350–500	50	200–600	20	No
Fe-air	5–10	60–80	45	300	20	No

Table 2
Advantages and disadvantages of selected aqueous batteries [17,27,31,88–91].

Technology	Advantages	Disadvantages
Pb acid	Abundant raw materials – low cost	Low energy density, limited cycle life, toxicity
NiFe	Long cycle life and abundant raw materials	Low energy density, low efficiency, self-discharge
Ni–Cd	Moderate energy density and moderate coulombic efficiency	Memory effects (relatively short life cycle), toxicity
NiMH	Moderate energy density	Memory effects (relatively short life cycle), low efficiency
Li-ion ($LiMn_2O_4/VO_2$)	High energy density, high round-trip efficiency, relatively long cycle life	High cost, safety issues, low Li abundance
Na-ion (λ-MnO_2/C)	High energy density, high round-trip efficiency, relatively long cycle life.	Little information – earlier development stage
Zn-air	High energy density, low cost, environmental friendliness, abundant raw materials, easy to scale up.	Short cycle life, low efficiency, self-discharge
Fe-air	Low cost, environmental friendliness, abundant raw materials, easy to scale up	Low coulombic efficiency, low energy density, self-discharge

disadvantages of the aqueous batteries presented in the previous sections.

3. Experimental section

3.1. Case study

Section 2.2 presented several reasons favouring the use of NiFe batteries, but also discussed some of the challenges associated with this chemistry. A major challenge preventing NiFe batteries from wider adoption is their low coulombic efficiency, which mainly occurs due to electrolyte decomposition during charging. Consequently, we have investigated several aspects of the behavior of iron based electrodes in such cells, and have developed NiFe batteries exhibiting coulombic efficiencies reaching 95%, whereby electrolyte decomposition has been virtually prevented [62,69,92–94].

3.2. Experimental details

Iron based electrodes were prepared procedures as described elsewhere [69,92,93]. Briefly, electrodes were produced by mixing varying amounts of Fe, FeS, Cu, Bi and Bi_2S_3 with PTFE. Strips of nickel foam (10 mm × 40 mm × 1.8 mm) were coated with the electrode materials and then hot-pressed at 150 °C and 10 kg cm^{-2} during 3 min, in such manner that 0.2–0.25 g of iron powder were loaded on an area of approximately 1 cm^2. Once produced, electrodes were tested in different electrolyte systems so coulombic efficiency was increased. As with the development of electrolyte systems, experimental design was used to facilitate the improvement of electrode formulations. Data extraction was automated by using an in-house developed C/C++ program that interrogates all files produced by the battery cycler. Data analysis was accomplished by utilizing Python and the R statistical software.

The basic electrolyte used in NiFe battery development is an aqueous solution of potassium hydroxide, typically at a molarity of 5.1 mol l^{-1}. Additives investigated in electrolyte formulations include, K_2S, LiOH, Mucic acid, $CuSO_4$, and selected thiols. Deionized water was produced by using an Elix 10-Milli-Q Plus water purification system (Millipore, Eschborn, Germany).

Iron-based electrodes were tested in a three-electrode cell with potentials measured against a mercury/mercury oxide (Hg/HgO) reference electrode ($E_{MMO}^0 = +0.098$ V vs. NHE). Nickel electrodes, obtained from a commercial nickel iron battery, were employed as counter electrodes. Electrodes were cycled from 0.9 to 1.4 V vs. Hg/HgO at a rate of C/5, which is a standard procedure for testing iron electrodes under galvanostatic conditions, by using an Arbin SCTS battery cycler. Galvanostatic charge discharge experiments were performed at room temperature until steady state was reached. Formation and stabilization of the electrodes was typically found to be complete by the 30th cycle of charge and discharge [62,93].
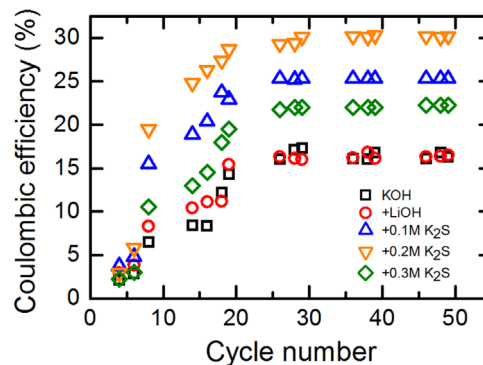

Fig. 3. Electrolyte systems for NiFe cells. Electrode formulation 80% Fe + 15% FeS + 5% PTFE. Electrolyte system formulation: (A) 5.1 M KOH, (B) 5.1 M KOH + 0.1 M LiOH, (C) 5.1 M KOH + 0.1 M K_2S, (D) 5.1 M KOH + 0.3 M K_2S, and (E) 5.1 M KOH + 0.2 M K_2S.

3.3. Results and discussion

3.3.1. Electrolyte formulation

Once assembled, NiFe cells were cycled as explained in Section 3.2. Experimental results indicate that before a NiFe battery attains a steady capacity, iron based electrodes require to reach a stable configuration before the steady state was reached. Fig. 3 illustrates that electrodes require such conditioning period however the electrolyte. It can be clearly seen that in the early stages (before the 10th cycle), coulombic efficiency is always very poor; however, this issues disappear with the cycle number and in general, after the 30th cycle, batteries have not only increased their coulombic efficiency, but have reached steady state.

In our previous paper [69], we have reported the use of lithium hydroxide seems to have a marginal incidence on cell performance (or at least for short term testing – less than 100 cycles of charge and discharge). Fig. 3 confirms this observation. It is noteworthy that the efficiency of electrolytes A and B (KOH and KOH + LiOH respectively) do not exhibit meaningful differences between them. It has long being recognized the use of lithium hydroxide as an electrolyte would benefit the long run operation of the iron electrode (increased electrode stability). However, our experimental tests were not long enough to either confirm or deny the veracity of this claim. Longer testing would reveal the usefulness of LiOH as an electrolyte additive for NiFe cells. Potassium sulfide is seen to have a positive effect on battery performance. The efficiency of formulations C, D and E are markedly higher than cells using electrolytes that did not contain potassium sulfide, and the greatest efficiency is observed at a K_2S molarity of 0.2 mol l^{-1} increasing the molarity of K_2S to 0.3 mol l^{-1} results in a significant reduction in efficiency, indicating the presence of an optimal molarity.
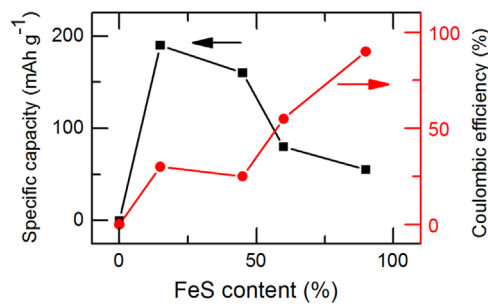
Fig. 4. Electrode systems for NiFe cells. Electrolyte formulation 5.1 M KOH+0.2 M K₂S.

3.3.2. Electrode formulation

Traditionally, iron electrodes have been manufactured by utilizing different additives, an in particular, the use of iron sulfide in concentrations not exceeding 15% has been reported to be beneficial to the performance of the battery [92], and in fact battery performance tend to decrease with the iron sulfide content in the region from between fifteen and forty percent of iron sulfide. Although, most NiFe papers tend to focus on electrode formulations below 20% FeS, we investigated the entire composition space of electrodes ranging from pure iron electrodes (0% FeS) to pure iron sulfide electrodes (100% FeS) on a binder free basis.

Fig. 4 illustrates the variation of capacity and coulombic efficiency with changing iron sulfide content. At concentrations of greater than 50% FeS, coulombic efficiency rises with FeS content; surprisingly coulombic efficiencies of 90–95% were reached when the iron sulfide content exceeded 80%, indicating that electrolyte decomposition has been prevented. However, Fig. 4 also shows that at high concentrations of iron sulfide, the capacity of the battery is drastically reduced in comparison with that achieved at low FeS concentrations.

Fig. 4 highlights the existence of compromise in battery design; at low concentrations of FeS coulombic efficiencies are low and capacities large conversely, at high FeS concentrations, coulombic efficiency tends to be high but capacity low. An additional problem with batteries utilizing large amounts of iron sulfide is their reduced life cycle. It was observed that cells utilizing large amounts of FeS faded after only 100–150 cycles. It remains a challenge to maintain the improved coulombic efficiency of NiFe batteries that utilize large fractions of FeS while improving capacity and cycle life.

4. Conclusions

By pursuing the development of cost effective iron sulfide based NiFe cells, we have identified two main electrode formulation regions. At low concentrations iron sulfide (below 30%), cells exhibit low coulombic efficiencies (20%) and relatively large capacities (190 mAh g^{-1}). Conversely, at large concentrations of iron sulfide, cells exhibit very large coulombic efficiencies (90%) and very low capacities (60 mAh g^{-1}).

The experimental approach used in this project, has facilitated and accelerated the development of secondary NiFe batteries. From our experimental findings, we can conclude there is a link between electrode performance (coulombic efficiency) and:

- electrode composition, in the form of iron sulfide content,
- electrolyte composition (presence of potassium sulfide), and
- life cycle.

A strong correlation between cell performance and electrolyte system was found. Potassium sulfate was identified as a key additive to improve cell performance. Lithium hydroxide on the other way was found to have limited effect in improving cell performance; however,

no long run testing was done, and it is not wise to rule out the importance of this additive that is present in nearly all NiFe cell formulations, so extended testing of the battery is recommended as a future work.

For large-scale applications, the safety and low installed costs of aqueous-based batteries make them desirable propositions if some of their limitations can be overcome. Due to the existing manufacturing capacity, lead acid cells are likely to remain a viable option for many applications, however as this is a mature technology; only incremental advances in performance are likely. More substantial improvements in performance with respect to efficiency, longevity and cost are likely to be seen in other aqueous-based chemistries, and these technologies have the potential to be integral components in future electricity supply systems.

Finally, the ideal aqueous battery would be one that had the longevity of a NiFe cell combined with the specific energy density of a metal air battery and the environmental friendliness of a 'rocking chair' battery. Developmentally daunting, but a worthwhile project requiring Manhattan Project-scale investments.

Conflict of interests

The authors declare that there is no conflict of interest regarding the publication of this paper.

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