Multiple regression analysis in the development of NiFe cells as energy storage solutions for intermittent power sources such as wind or solar

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A B S T R A C T

Multiple regression analysis was used to investigate the effect of bismuth sulphide and iron sulphide as anode additives for NiFe cells. With this in mind, in-house made Fe/FeS/Bi_2S_3 based electrodes were cycled against commercially available nickel electrodes. A simplex centroid design was used to investigate the combined effects of any of the aforementioned additives on cell performance. The manuscript ends with an initial look at electrolyte systems as a means to further improve the performance of our cells. Finally, our findings support the idea that HS- ions improve the overall performance of NiFe cells.

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Introduction

Although, there is a continuously increasing demand of energy coming from renewable sources; the intermittent nature of these resources restrict their use (temporary wind profiles, availability of sun light, sufficient/constant supply of water, etc); so energy generation and demand are not easily matched [1—5]. Nonetheless, we are facing a transition to integrate an increasing share of energy coming from renewable sources to balance the electric grid [6—16]. Three different strategies have been proposed to tackle the aforementioned problem: energy storage, transmission and full back up capacity (for example by using fossil fuels); this manuscript looks at NiFe batteries as a means to store large amounts of energy coming from intermittent power sources such as wind or solar.

Among all renewable sources, wind power is, undoubtedly, one the world's fastest growing technologies [3]. It is well known that offshore wind is stronger and steadier than its onshore counterpart, so offshore wind farms could convert larger amounts of wind energy into more useful forms of energy (such as electricity) [10,17—19].

Unfortunately, large scale energy storage is still very expensive and inefficient. Broadly speaking, energy storage demands electricity to be converted into some non-electrical form of energy which must be reverted back into electricity for further use. This process is not 100% efficient and prices are still very high. Compared with our current technologies, a more practical way to store large amounts of energy is very much needed. This is because, unfortunately, modern batteries would utilize:

- organic/flammable electrolyte systems
- ultrapure and/or non-abundant (costly) reactants
- environmentally unfriendly raw materials and components
- costly nano-structuring procedures

These aspects will increase the price of the battery and would polarize general opinion against large scale implementation of the intended solution.

NiFe cells are rechargeable aqueous batteries that were successfully commercialized by Edison back in the early 20th century. Although, this technology was superseded by cheaper (and more toxic) lead-acid cells, there is a renewed interest on them, arising from their environmental friendliness, low cost of raw materials, long life and tolerance to electrical abuse (such as overcharge, over-discharge, being idle for extended periods and short-circuit conditions) and compatibility with intermittent power sources, such as wind power and photo-voltaic's (PV's). In addition, this technology would be suitable for relatively low specific energy applications (30–50 Wh kg^{-1}) [20].

The low cost and abundance of the raw materials required to produce NiFe cells are two important aspects that further encourage their use. Iron is the fourth most abundant element in the Earth's crust [21,22]. Nickel is less abundant than iron, but it is still relatively abundant [23,24]. Other materials/compounds such as potassium hydroxide, sulphur and iron sulphide are also very abundant [25–28]. Bismuth is relatively scarce [29,30] but only small amounts of it are required to produce NiFe cells. Basically, there are not good reasons to foresee a shortage of any of the aforementioned elements any time soon.

There are, of course, many challenges preventing a large scale utilization of NiFe cells for offshore wind applications, such as low cell efficiency, electrolyte decomposition (hydrogen evolution), and low energy and power densities [31,32]. Essentially, the major challenge preventing this technology from becoming a real solution to the large scale energy storage problem is the low round trip performance of the battery, which is strongly related to the evolution of hydrogen via decomposition of water on the surface of the iron electrode. So from our point of view, the evolution of hydrogen is something we must reduce, minimize or even prevent rather than enhance; this is, we are not interested in storing and utilizing the hydrogen that is produced during the charging of the battery, even though we could look at different ways of utilizing such resource [33–35].

Under strong alkaline conditions, the main process taking place during the charging of an iron electrode is the reduction of ferrous ions (Fe^{2+}) to metallic iron (Fe^0); conversely, during discharge, metallic iron is oxidized to ferrous ions. Eq. (1) illustrates the charging and discharging (forward and backward reactions respectively) processes of an iron electrode under alkaline conditions [32,36].

$$Fe(OH)_2 + 2e^- \leftrightarrow Fe + 2OH^- \quad E^0 = -0.87V \quad (1)$$
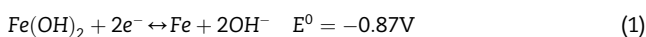
Unfortunately, during the charging of the battery, water is electrochemically decomposed into hydrogen and hydroxyl ions. Because of that, part of the energy that is intended to be stored in the battery, ended up wasted in the parasitic evolution of hydrogen. Hydrogen evolution, therefore, accounts for a drastic reduction in the overall performance of the battery, as indicated by Eq. (2).

$$2H_2O + 2e^- \leftrightarrow H_2 + 2OH^- \quad E^0 = -0.83V \quad (2)$$
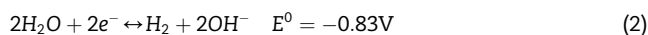
The evolution of hydrogen on the surface metals under alkaline conditions is a subject of paramount importance in modern times [37,38]. In particular on the surface of iron, as illustrated by Eq. (2) reflect the importance of this reaction, but from a detrimental point of view [39–41]. There are plenty of situations where enhancing the evolution of hydrogen is desired, however, in the realm of NiFe batteries the problem is exactly the opposite. It is crucial to reduce, minimise or even prevent this reaction.

The prevention of electrolyte decomposition has been achieved by modifying the iron electrode by either nano-structuring the anode or by the addition of elements (such as sulphur or bismuth), in such a way that the overpotential for hydrogen evolution was increased [42,43]. Electrolyte modification also permits preventing Eq. (2) from happening. In fact, different electrolyte additives such as wetting agents [44], long chain thiols [45], etc., have been investigated for such end [42]. With this in mind, NiFe batteries with exceptional capacities of nearly 800 mAh g^{-1} have been reported [46,47]. Although, highly efficient, these batteries require costly reactants and nano-structuring techniques. These aspects would certainly influence the final price of the battery [46,47].

In our previous publications, the role of selected electrode additives (such as bismuth and iron sulphide) on battery performance has been explored [43,48]. Our experimental findings suggested that bismuth sulphide and iron sulphide effectively improve the performance of the NiFe cell. However, the remaining question is whether a synergistic effect between them would exist. Conventional NiFe battery research would consider one single electrode additive at a time, thus neglecting the occurrence of combined effects, this is, situations where the combined effect of the factors is greater than the sum of the parts. This manuscript ends with an initial look at electrolyte selection and improvement.

Experimental

By using a similar procedure as the one described in our previous publications [17,43], iron based anodes were produced by using varying amounts of Fe, PTFE, FeS and Bi$_2$S$_3$. Essentially, strips of nickel foam (10 mm × 40 mm × 1.8 mm) were coated and then vacuum dried until approximately 0.2–0.25 g of iron powder were loaded on an area of approximately 1 cm^2. The chemicals and materials used were of the following specifications.

- Iron powder (purity 99.5%, <10 μm) from Alfa Aesar
- Iron sulphide (purity 99.5%) from Sigma Aldrich
- Bismuth sulphide (purity 99.5%, <5 μm) from Sigma Aldrich
- PTFE (Teflon 30-N, 59.95% solids) from Alfa Aesar
- Nickel foam (purity 99.0%, density 350 gm^{-2}) from Sigma Aldrich

- Potassium hydroxide (purity $\geq$ 85.0%, pellets) from Sigma Aldrich
- Potassium sulphide (purity $\geq$ 99.5%) from Sigma Aldrich
- Lithium hydroxide (purity $\geq$ 98.0%) from Sigma Aldrich

In house deionized water was produced by using an Elix 10-Milli-Q Plus water purification system (Millipore, Eschborn, Germany). Basically, varying amounts of electrolyte components were dissolved in our in-house produced deionized water. The electrolyte system used for electrode development consisted of an aqueous solution of 5.1 M KOH.

Our previous experimental results have proven the usefulness of PTFE as a means to produce a conductive iron based ink [49], we have kept the composition of PTFE at a constant value of approximately 6%$_w$. Based on the constancy of the binder and our desire to explore the composition space defined by formulations not exceeding 15%$_w$ on each additive, Table 1 was constructed.

By using six replicates per electrode formulation and the two standard deviation criteria for rejection, a surface response model that allows the finding of electrode formulations that reduce electrolyte decomposition was obtained.

Broadly speaking, electrolyte systems for NiFe cells are concentrated solutions of potassium hydroxide and other minor constituents, we decided to keep the concentration of KOH constant (5.1 M), and to explore the combined effect of lithium hydroxide and potassium sulphide (six replicates per electrolyte formulation were used). Table 2 reports electrolyte systems under consideration.

The electrode and electrolyte formulations were tested on a three electrode cell. In-house made anodes were tested in a three-electrode cell. Nickel electrodes, obtained from a commercial nickel iron battery, where used as cathodes. All potentials were measured against a mercury/mercury oxide (Hg/HgO) reference electrode ($E^0_{Hg/HgO}$ = +0.098 V vs. NHE).

Experiments of charge and discharge were conducted on a 64 channel Arbin SCTS battery cycler under galvanostatic conditions at room temperature until the steady state was reached. Cells were cycled from 0.6 to 1.4 V vs. Hg/HgO at a C/5 rate. Formation and stabilization of the electrodes were found to be complete by the 30th cycle of charge and discharge [43,48,49]. Fig. 1 provides a sketch of the cell test configuration.

Results and discussion

Electrode formulation

It has been recognised that any NiFe cell requires a relatively long conditioning period (in the order of 30 cycles of charge

Table 1 – Experimental determinations of factors and levels (free-PTFE basis).

Factor	Concentrations (%$_w$)	
	Low	High
Fe	70	100
FeS	0	15
Bi$_2$S$_3$	0	15

Table 2 – Electrolyte systems under consideration.

System	Composition
S1	5.1 M KOH
S2	5.1 M KOH + 0.1 M LiOH
S3	5.1 M KOH + 0.1 M K$_2$S
S4	5.1 M KOH + 0.1 M LiOH + 0.1 M K$_2$S

Table 3 – Experimental design matrix (PTFE-free basis, electrolyte system S4, 50th cycle).

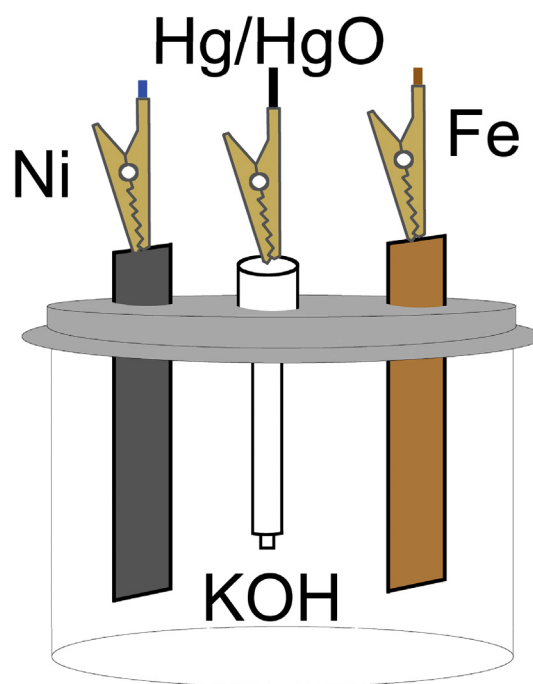| Cell	%$_w$FeS	%$_w$Bi$_2$S$_3$	η_Q^{Exp}	η_Q^{Model}
A	7.5	15.0	43.5 ± 2.3	43.2
B	7.5	7.5	47.0 ± 1.2	46.6
C	7.5	0.0	42.9 ± 2.4	42.2
D	0.0	7.5	28.5 ± 2.3	26.9
E	15.0	7.5	45.7 ± 1.8	45.8
F	12.8	12.8	48.3 ± 3.0	46.5
G	12.8	2.2	46.1 ± 2.3	45.9
H	2.2	12.8	32.6 ± 1.9	33.2
I	2.2	2.2	32.4 ± 1.9	32.5

Fig. 1 – Test cell configuration.

and discharge) before it reaches the steady state [17,43,48]. Fig. 2 confirms this observation.

Based upon Table 1, and by using the mixing rules in a three dimensional concentration space, a simplex centroid design based on a conventional central composite design was proposed. Table 3 reports experimental values of coulombic efficiency calculated for our electrodes developed by considering Table 1 and utilizing electrolyte system S1. It is important to note that collected data exhibit large variability so a relatively large number of replicates (six in this case) were used to increase the statistical force of the analysis. With this in mind, any sample whose coulombic efficiency lays more than two standard deviations from the mean was rejected.
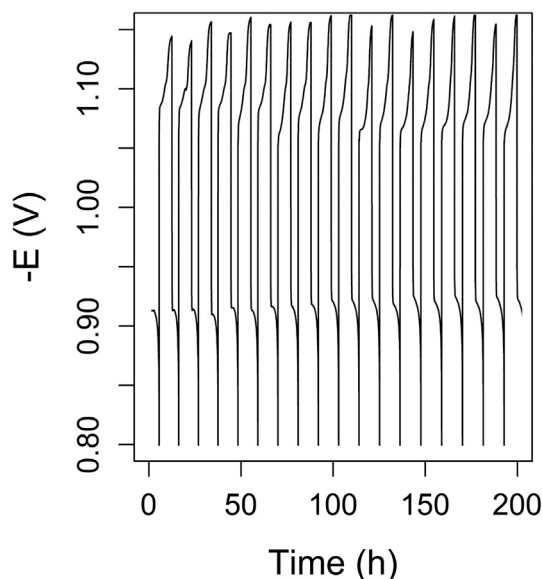
Fig. 2 – Galvanostatic charge and discharge profile for a NiFe cell (sample F from Table 3, electrolyte system S1 from Table 2) versus mercury/mercury oxide (Hg/HgO) reference electrode.

In order to determine whether a relationship existed between the factors and responses (coulombic efficiency and electrode additives), polynomial functions, as the one represented by Eq. (3) were used

$$\eta_Q = \sum_{i=1}^{n} \sum_{j=0}^{m} \left[\alpha_{i,j} Y_i^j \right] \qquad (3)$$

Where η_Q represents coulombic efficiency, the α terms are the expansion coefficients, the Y terms represent the weigh per-cent of each component, n the number of component in the electrode formulation and m is the order of the polynomial.

We began by investigating the simplest forms of Eq. (3) until the predicted by the model coulombic efficiencies closely mirrored the experimental values. The response coulombic efficiency was explained by the composition factors. The final quadratic model is represented by Eq. (4):

$$\eta_Q = 22.514 + 3.996\ Y_{FeS} + 1.117\ Y_{Bi2s3} - 0.183\ Y^2_{FeS}$$
$$- 0.0702\ Y^2_{Bi2s3} \qquad (4)$$

The regression analysis reveals not only a relatively high multiple correlation coefficient ($r^2 = 0.9533$), but also a highly significant model (F statistic 250.2), and as expected, all terms from the model are significant. Finally, no evidence against normality was found.

Note that at first glance, Eq. (4) seems to ignore the composition of iron in the electrode formulation. But this observation is not correct, for all components within each formulation must add up to 100%. The model establishes that iron, as an electrode component (factor) is not significant. This can be rationalised in terms of its dominance within the formulations, for iron accounts for at least 70% of the electroactive material.

It is important to recognise that although, large variability on cell performance was always noted, the second order model given by Eq. (4) renders a relatively good fit, and this is because by increasing the number of replicates, the likelihood of having used true values is enhanced. Fig. 3 provides a three dimensional representation of Eq. (4).

We are not going to give a presentation on how to find the maximum value of a differentiable function subject to a constraint (such as %Bi$_2$S$_3$ + %FeS + %Fe = 100). The details of such procedure can be found in most books of calculus, and this subject is out of the scope of this manuscript. The final electrode formulation that reduces electrolyte decomposition was found to be 10.3% FeS + 7.5% Bi$_2$S$_3$ + 76.5% Fe + 5.7% PTFE, and was denoted by formulation M.

Electrolyte system

Now that we have developed an electrode formulation that renders low electrolyte decomposition, the next step is to investigate which electrolyte system would further reduce hydrogen evolution without adversely affecting cell performance. Our strategy is to use our newly found electrode formulation M to find an electrolyte formulation that further enhances cell performance.

As was explained in the introduction, electrolyte systems for NiFe cells, consist of aqueous solutions of concentrated KOH (in the order of 5.0 M) and lithium hydroxide. It has been reported that the soluble bisulfide anion (HS$^-$) would increase the performance of the NiFe cells by mitigating electrolyte decomposition; however, our previous experimental results have shown that this is not entirely correct, for at low concentrations, the performance of the cell seems to be independent of the presence of this additive [17,48], but this aspect require further investigation. In order to do that, we are going to compare electrolyte formulations and then we will find out whether or not meaningful differences in battery performance exist.

Fig. 4 compares electrolyte formulations (from Table 2) based on groups of 6 replicates per formulation. Each group
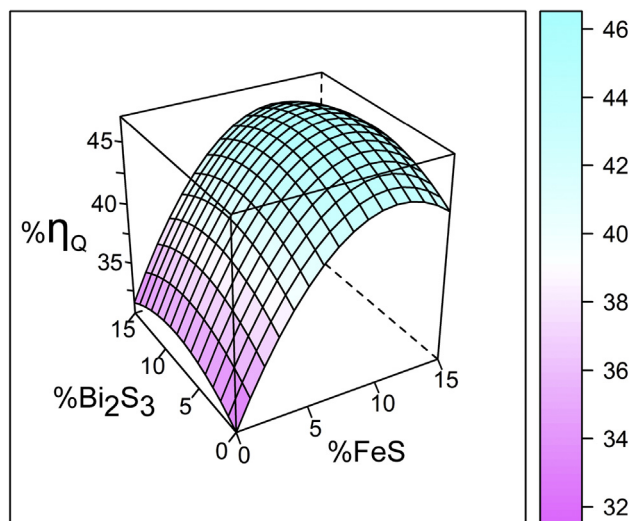

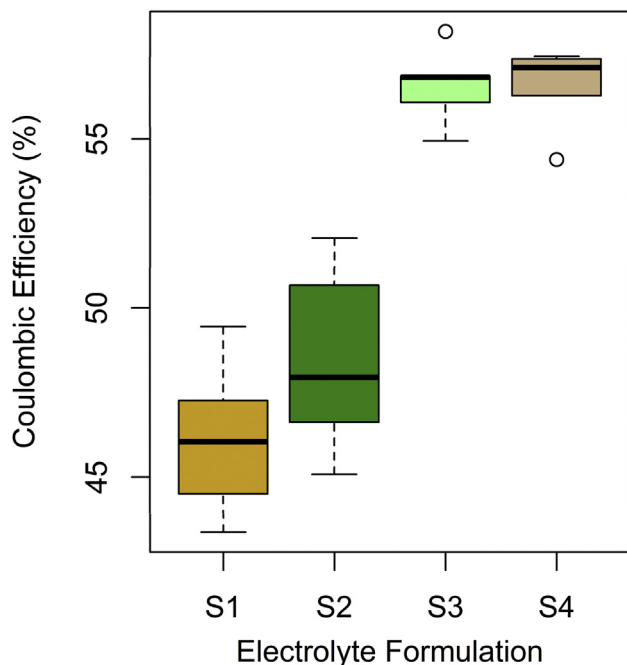**Fig. 3 – Second order coulombic efficiency representation.**

Fig. 4 – Battery performance (electrode formulation M) as a function of electrolyte formulation. For information on electrolyte system composition, please refer to Table 2.
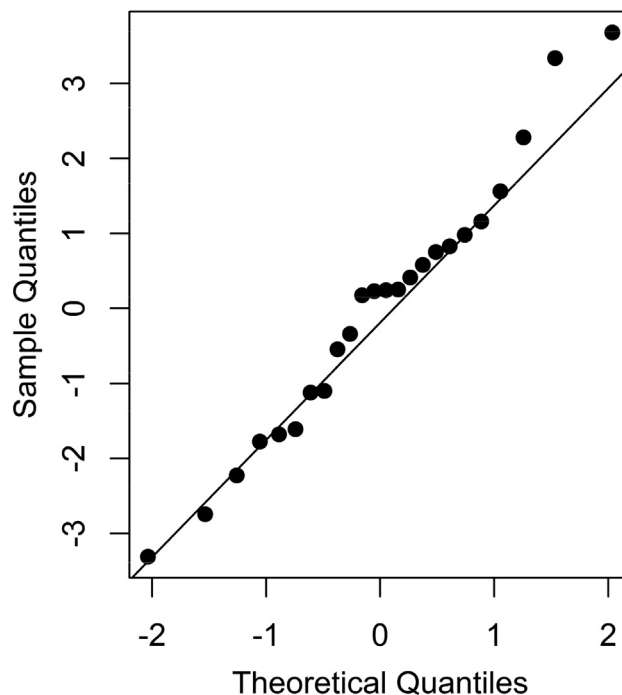

Fig. 5 – Normal probability plot for coulombic efficiency residuals.

corresponds to a different box; each horizontal line within the box represents the mean coulombic efficiency for that formulation. Likewise, whiskers indicate extreme values and empty circles outliers (data that lays more than two standard deviations from the mean).

A visual inspection of Fig. 4 reveals that plain potassium hydroxide as electrolyte (formulation S1) is outperformed by any of the remaining electrolyte systems. It seems clear that both lithium hydroxide and potassium sulphide increases the performance of the NiFe cells. Although, these conclusions seem to be logical, we require a more formal way of drawing conclusions. In this case, we are going to use the Tukey's HSD to find out whether meaningful differences across electrolyte formulations exist.

To begin with, we must check that our data is normally distributed; a residuals analysis indicates no evidence against normality. As shown in Fig. 5, data are randomly dispersed and a linear regression model is appropriate for the data.

The same conclusion can be drawn by using more rigorous normality tests, such as the Shapiro–Wilk (SK) or Kolmogorov–Smirnov test (KS test), which are nonparametric tests for normality. In this case the both tests consolidate the lack of evidence against normality, as all p-values are significant (data not shown).

The Tukey HSD test reveals no meaningful differences among electrolyte systems S1 and S2 or between S3 and S4. The results are shown in Fig. 6.

The practical implications of the fact that there are meaningful differences neither between formulations S1 and S2 nor between S3 and S4 are tremendous, for they imply that lithium hydroxide does not meaningfully enhance the performance of the battery (well, not at least under our experimental conditions). It is important to mention here that it has

been suggested that lithium hydroxide would enhance the cycling life of the battery; this claim, of course, would require long testing and it is propose as a future work.

Unlike lithium hydroxide, the Tukey-HSD reveals the use of potassium hydroxide does indeed enhance battery
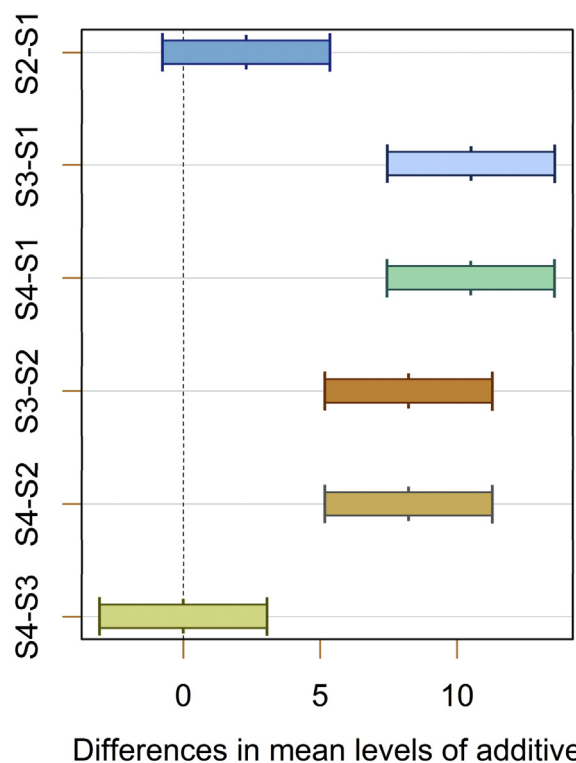

Fig. 6 – 95% family-wise confidence level.

performance. From this statement, it necessarily follows that soluble species coming from the aforementioned reactant would be responsible for the prevention of electrolyte decomposition and thus the evolution of hydrogen. It has been proposed that the soluble bisulphite anion (HS^-) is indeed responsible for such behaviour. And our experimental results are in-line with such claims.

Fig. 7 confirms the tendency described in Fig. 2, in the sense that battery performance tends to increase with the cycle number during the conditioning period (first 20–30 cycles). Moreover, battery performance tends to increase in a rather unpredictable manner; however, in the long run, the performance of the battery would increase until the steady state was reached (this is taken as the end of the conditioning period). The authors believe this is because electrodes tend to fall apart until they reached a stable configuration where they can handle the current requirements of the charge/discharge test without major structural changes.

Finally, a large specific charge storage capacity close to 290 mAh g^{-1} was observed. Although, larger capacities (close to 800 mAh g^{-1}) have been reported [46,50–52], our manufacturing process is a more cost-effective solution, for it only utilises commercial grade reactants, which makes it ideal for grid-scale energy storage applications.

The renewal of metal surface area on iron materials has been identified as a key parameter in the evolution of hydrogen under strong alkaline conditions [53,54]. We believe, therefore, that due to the breaking up of the electrode, new electrode surface area is available for the electrochemical reactions to take place.

Conclusions and future work

By pursuing the development of cost effective offshore wind energy storage, aqueous based NiFe batteries with coulombic
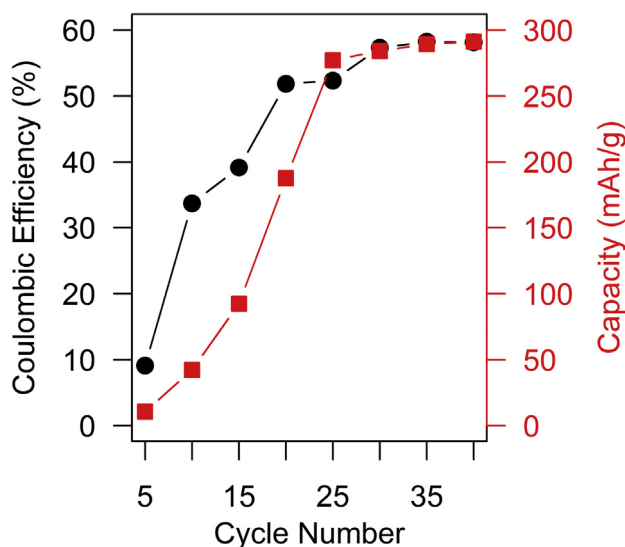

Fig. 7 – Battery performance versus cycling number for NiFe cell formulation (electrolyte system S4 and anode formulation M). Key: circles coulombic efficiency, squares capacity.

efficiencies in the order of 58% and capacities in the order of 290 mAh g^{-1}. These results are very promising as we have used neither ultra-pure reactants, nor we have nanostructured the electrode, so our batteries hold a promise for a real cost effective solution to store large amounts of energy coming from intermittent sources such as wind power.

The experimental approach used and explained in this manuscript has been successful in facilitating the development and improvement of secondary NiFe cells, by reducing electrolyte decomposition and thus hydrogen evolution. The formulation developed corresponds to an iron electrode formulation consisting of 10.3% FeS + 7.5% Bi_2S_3 + 76.5% Fe + 5.7% PTFE. It was also found that the aqueous electrolyte 5.1 M KOH + 0.1 M $LiOH$ + 0.1 M K_2S further reduced the evolution of hydrogen, thus improving the overall performance of the aqueous NiFe cell.

It was found that under our experimental conditions, potassium sulphide has a real incidence on the performance of the battery; in other words, the presence of potassium sulphide in the electrolyte increases coulombic efficiency. This conclusion also supports the idea that the soluble bisulfide anion (HS^-) do improve the overall performance of NiFe cells.

From our experimental findings, we can conclude there is a link between electrode performance (coulombic efficiency) and:

- conditioning of the iron electrode (development of new surface area)
- electrode composition
- electrolyte composition (presence of potassium sulphide)

The data gathered during this project is subject to large variability; therefore, a relatively large number of replicates (6 in total) and the two standard deviation criteria for rejection were used to increase the statistical force of the analysis.

Our experimental findings would suggest that at the level of confidence $\alpha = 0.05$, potassium sulphide, as electrolyte additive, does enhance the performance of the battery.

Finally, the evidence for lithium hydroxide supports the idea that this additive only marginally improves cell performance. However, it has been reported that in the long run, LiOH would enhance cycle life and round trip efficiency, so extended testing is recommended as a future work.

Acknowledgements

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