



# Post-hoc comparisons among iron electrode formulations based on bismuth, bismuth sulphide, iron sulphide, and potassium sulphide under strong alkaline conditions



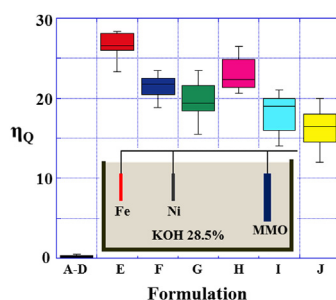
Jorge Omar Gil Posada<sup>\*</sup>, Peter J. Hall

Chemical and Biological Engineering, University of Sheffield, Sir Robert Hadfield Building, Mapping Street, Sheffield S1 1XJ, England, UK

## HIGHLIGHTS

- We investigate sulphur containing additives in the performance of NiFe cells.
- We perform post-hoc comparisons among NiFe cell formulations.
- The performance of a NiFe cell depends on the initial cycles of charge/discharge.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 30 April 2014

Received in revised form

6 June 2014

Accepted 23 June 2014

Available online 7 July 2014

### Keywords:

NiFe cell

Post-hoc comparison

Coulombic efficiency

Iron electrode

## ABSTRACT

Iron electrodes were prepared by hot-pressing iron-polyethylene based formulations on nickel foam stripes. NiFe cells were tested by using commercial nickel electrodes and our iron electrodes. Post-hoc comparisons were used to identify meaningful differences between iron electrode formulations (based upon bismuth, bismuth sulphate, potassium sulphide and iron sulphide as additives). Our results confirm that both bismuth sulphide and iron sulphide favour the process of charge/discharge of a NiFe cell. In addition, we have found that the use of metallic bismuth only marginally influences coulombic efficiency; likewise, the presence of the soluble bisulfide anion is not sufficient to increase coulombic efficiency. Finally, NiFe cells prepared with bismuth sulphide outperformed their iron sulphide counterparts.

© 2014 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/3.0/>).

## 1. Introduction

NiFe cells are aqueous rechargeable batteries where the iron electrode forms the anode while the nickel electrode constitutes the cathode. Basically, in these cells, the aqueous electrolyte is a concentrated solution of KOH.

Historically, NiFe cells have been commercialised since the 1900's and due to their robustness, longevity and relatively simple chemistry, scientists believe these batteries could be a low cost solution for energy storage in applications where relatively low specific energy (in the order of 30–50 Wh kg<sup>-1</sup>) is required.

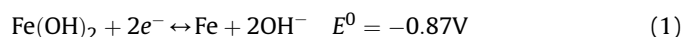
There are many challenges preventing a large scale utilization of NiFe cells, such as relatively low efficiency, considerable evolution of hydrogen, low energy and power densities [1,2].

Ideally, the main process taking place during the charging of an iron cell should be reduction of iron (II) to metallic iron; likewise, the oxidation of metallic iron to iron (II) should take place during

<sup>\*</sup> Corresponding author. Tel.: +44 01142228257; fax: +44 01142227501.

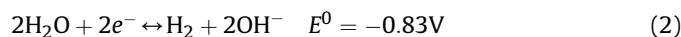
E-mail addresses: [j.o.gil-posada@sheffield.ac.uk](mailto:j.o.gil-posada@sheffield.ac.uk), [jogp1234@yahoo.com](mailto:jogp1234@yahoo.com) (J.O. Gil Posada).

the discharging process [2,3]. These two process are represented by Eq. (1).



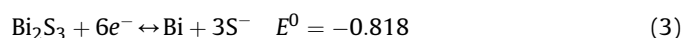
In our present discussion, the forward reactions occur during the charging of the iron electrode; in a similar way, reverse reactions take place during the discharging of the electrode.

Unfortunately, it is well known that under strong alkaline conditions water is decomposed into hydrogen during the charging of an iron electrode; therefore, part of the charging current is wasted in producing hydrogen thus lowering the overall coulombic efficiency of the cell, as illustrated by Eq. (2).



Many attempts have been made in order to improve the performance of NiFe cells. While NiFe cells with staggering capacities of nearly 800 mAh g<sup>-1</sup> has been produce by nano-structuring the iron electrode [4,5]; it is thought that a more cost effective formulation is still needed, and indeed, we have demonstrated in our recent publication that NiFe cells could provide a low cost alternative for energy storage [6]. With this in mind, we have started with the development of catalytic systems that not only foment the charging process of the iron electrode, but that minimize the evolution of hydrogen under strong alkaline conditions.

Undoubtedly, bismuth sulphide has been extensively investigated for its potential to reduce the evolution of hydrogen while increasing the charging efficiency of NiFe cells. It has been proposed that during the charging of a NiFe cell, bismuth sulphide undergoes the following transformation:



It has been reported that metallic bismuth increases coulombic efficiency by decreasing the evolution of hydrogen in the iron electrode [5]. However, our experimental results suggest that metallic bismuth per se, is not necessarily responsible for preventing hydrogen evolution during the charging of a NiFe cell.

Nowadays modern research on iron electrodes for NiFe cells hinges on the suppression of hydrogen evolution, usually by the addition of sulphur containing additives (such as bismuth sulphide [5,6], thiourea [7], led sulphide and iron sulphide [8], among others [9–13]); likewise the use of wetting agents such as Triton X-100 has been reported to enhance the performance of the iron electrode [14]. In addition, the use of pore former additives, such as potassium carbonate, and depassivation agents, such as sodium sulphide, also play a major role in the development of highly efficient iron electrodes for NiFe cells [12]. In this article, we focus on the use of potassium carbonate as a pore former in conjunction with the addition of selected sulphur containing additives.

## 2. Experimental

Iron electrodes were produced by coating and hot pressing strips of nickel foam (10 mm × 40 mm × 1.8 mm) with an iron active paste which consists of varying amounts of carbonyl iron (electroactive material) with a mixture of polyethylene powder (acting as a binder) and potassium carbonate (which decompose during the hot-pressing process, thus creating porosity) with either of the following electrode additives: bismuth, potassium sulphide, bismuth sulphide or iron sulphide. The chemicals and materials used to produce the electrodes were of the following specifications.

- Carbonyl iron powder (purity 99.7%) from Alfa Aesar
- Polyethylene powder from Alfa Aesar

- Potassium carbonate (purity 99.0%) from Sigma Aldrich
- Bismuth sulphide (purity 99.5%) from Sigma Aldrich
- Iron sulphide (purity 99.5%)
- Potassium sulphate (purity 99.0%) from Sigma Aldrich

The procedure followed to produce our cells consists in the following steps:

- Electrodes were made of Ni-foam by cutting strips of 4 cm × 1 cm
- Electro-active pastes were produced by mixing varying amounts of Fe, FeS, K<sub>2</sub>S and Bi<sub>2</sub>S<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, and polyethylene powder (PP)
- Every Ni-foam electrode was coated with an electroactive paste (see below)
- Electrodes were hot pressed at 150 °C and 10 kg cm<sup>-2</sup> during 3 min
- Repeat steps iii-iv until a constant amount of electro-active material was loaded onto the electrode (approximately 0.2 g of paste were loaded on an area of almost 1 cm<sup>2</sup>)
- Cells were assembled and tested

As was previously explained, scientists believe that metallic bismuth could increase the hydrogen overvoltage potential thus reducing its evolution during the charging of an iron electrode. In order to clarify the role of elemental bismuth in lowering the evolution of hydrogen on a NiFe cell, different formulations were produced and compared against each other. Table 1 lists the electrode formulations investigated in this article.

Although, the formulations reported in Table 1 were selected based upon previous results, these formulations were not optimised (that would take too long). The assumption was that comparisons were possible in regions where formulations rendered NiFe cells with good performance. Note that in our recent publication, we developed a formulation that renders efficiencies in the order of 45% [6]. But our objective is to compare formulations, not to optimise them (at least, not for the moment).

The iron electrodes appearing in Table 1 were tested on a three electrode cell. The counter electrode was a large commercial nickel electrode (obtained from a commercial nickel–iron battery), so the cells were negative limited. The electrolyte was a concentrated solution of KOH (28.5%). Experiments of charge and discharge under galvanostatic conditions were conducted at room temperature until the cell reached the steady state. Cells were cycled from 0.6 to 1.4 V vs. MMO at a C/5 rate. Formation and stabilization of the electrodes were found to be complete by the 30th cycle of charge and discharge. More experimental details can be found elsewhere [6].

## 3. Results and discussion

Our experimental results clearly indicate that under alkaline conditions, neither metallic bismuth nor potassium sulphide would

**Table 1**  
Electrode formulations.

Cell	Composition (wt%)
A	90%Fe + 5% PP + 5% K <sub>2</sub> CO <sub>3</sub>
B	85%Fe + 5% Bi + 5% PP + 5% K <sub>2</sub> CO <sub>3</sub>
C	85%Fe + 5% K <sub>2</sub> S + 5% PP + 5% K <sub>2</sub> CO <sub>3</sub>
D	80%Fe + 5% Bi + 5% K <sub>2</sub> S + 5% PP + 5% K <sub>2</sub> CO <sub>3</sub>
E	85%Fe + 5%Bi <sub>2</sub> S <sub>3</sub> + 5% PP + 5% K <sub>2</sub> CO <sub>3</sub>
F	80%Fe + 5%Bi <sub>2</sub> S <sub>3</sub> + 5% Bi + 5% PP + 5% K <sub>2</sub> CO <sub>3</sub>
G	80%Fe + 5%Bi <sub>2</sub> S <sub>3</sub> + 5% K <sub>2</sub> S + 5% PP + 5% K <sub>2</sub> CO <sub>3</sub>
H	85%Fe + 5%FeS + 5% PP + 5% K <sub>2</sub> CO <sub>3</sub>
I	80%Fe + 5%FeS + 5% Bi + 5% PP + 5% K <sub>2</sub> CO <sub>3</sub>
J	80%Fe + 5%FeS + 5% K <sub>2</sub> S + 5% PP + 5% K <sub>2</sub> CO <sub>3</sub>

increase the performance of the iron electrode. It is well known that any NiFe cell requires a relatively long conditioning period (usually the less than the first 30 cycles of charge and discharge) to develop its full potential as an energy storage device. Fig. 1 illustrates how battery performance evolves with the cycle number.

Fig. 1 reveals that there is a conditioning period during which the cell gains performance (starting near zero coulombic efficiency). It is not surprising that some formulations exhibit a very poor performance (such as formulation A, corresponding to a plain iron electrode). From this figure, it necessarily follows that the additives used to produce formulations B, C and D only marginally improve the coulombic efficiency of the NiFe cells (as there are not meaningful differences between such formulations and a plain iron electrode, formulation A). On the other way, the use of formulations E, F, G, H, I and J will drastically improve the coulombic efficiency of the cells under investigation, and so we will have a closer look at such formulations. Note that the continuous lines that join points in Fig. 1 are used to facilitate the interpretation of the diagram; however, coulombic efficiency is not a continuous variable, for it is calculated for a given cycle.

Broadly speaking, Fig. 1 indicates that elemental bismuth, potassium sulphide and their mixtures do not have a real incidence on the iron electrode, unless additives such as bismuth sulphide or iron sulphide are also in the electrode formulation. Notice that it is virtually impossible to differentiate between electrode formulations A, B, C and D, as coulombic efficiency is negligible in each of them. Moreover, the presence of elemental bismuth and potassium sulphide seems to decrease coulombic efficiency when used as complementary additives for either bismuth sulphide or iron sulphide. Finally, it is also clear that electrode formulations based on bismuth sulphide outperform their iron sulphide counterparts.

We have found that the utilization of the electroactive material ( $U_Q$ ) is not improved by the addition of elemental bismuth, nor by the presence of  $K_2S$ . The term “electroactive material” refers to the electroactive material in the iron electrode (carbonyl iron in this case). Fig. 2 illustrates how the utilization of the electroactive material evolves with the cycle number.

Fig. 2 clearly indicates that there are clear differences between samples with and without metallic bismuth or  $K_2S$ . Moreover, it is also clear that electrode formulations that include bismuth sulphide over-perform their iron sulphide counterparts.

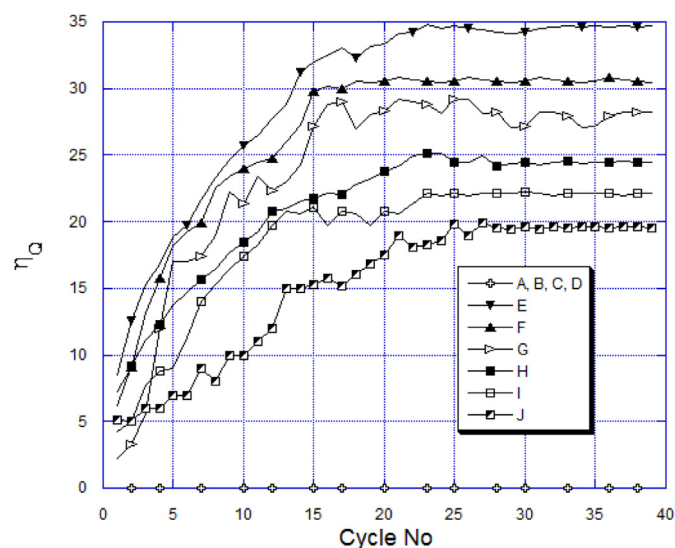


Fig. 1. Coulombic efficiency versus cycle number on selected NiFe cells. For details on compositions, please refer to Table 1.

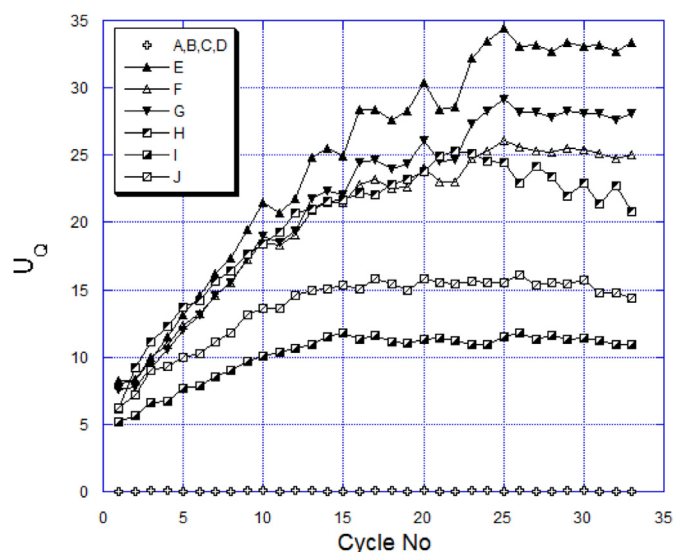


Fig. 2. Utilization of the electroactive material versus cycle number on selected NiFe cells. For details on compositions, please refer to Table 1.

Figs. 1 and 2 confirm the existence of a conditioning period that is required for each battery to reach its highest performance. In essence, during this period, both coulombic efficiency and utilization of electroactive material increase until they reach the steady state. Figs. 3 and 4 also confirm the existence of such conditioning period. From the observation of these two figures, it follows that whatever is happening during this period, is crucial to understand and explain the reactivity of the iron electrode.

Fig. 4 indicates that after the 30th cycle, there is good reproducibility for the curves of charge and discharge. And although, this is illustrated with formulation E, the same trend has been observed for all samples under investigation. From this figure, we can see a specific charge storage capacity of  $0.25 \text{ Ah g}^{-1}$ , which is a remarkable achievement, given the fact that we are using neither nano-

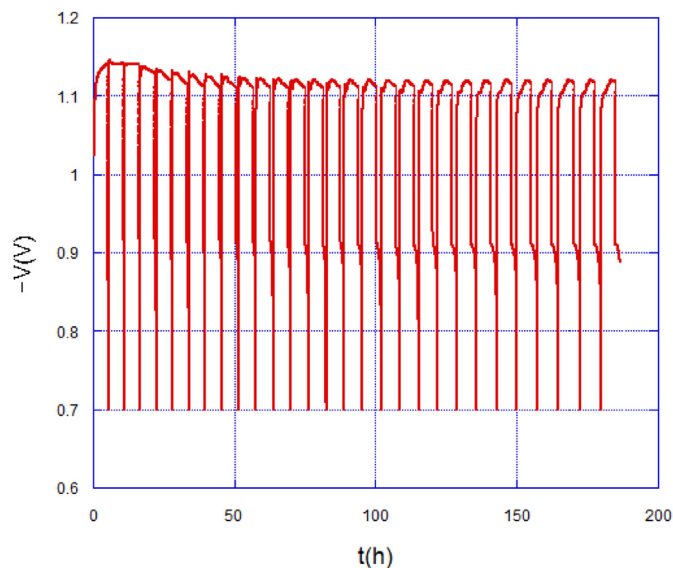
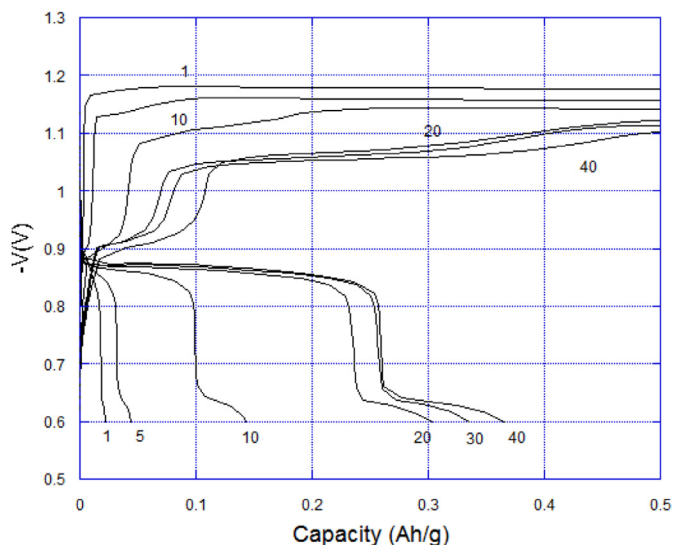


Fig. 3. Charge and discharge profile for a NiFe cell (sample E from Table 1) versus mercury/mercury oxide (MMO) reference electrode. Cells were cycled from 0.6 to 1.4 V vs. MMO under galvanostatic conditions at a  $C/5$  rate.



**Fig. 4.** Selected charge and curves for sample E (from Table 1) versus mercury/mercury oxide (MMO) reference electrode. The upper curves represent the charging of the electrode (cycles 1, 5, 10, 20, 30 and 40); likewise, the lower curves represent the discharging of the electrode (cycles 1, 5, 10, 20, 30 and 40).

structuring the iron electrode, nor ultrapure reactants (purity of carbonyl iron 99.7%). In comparison, formulations rendering 0.3 Ah g<sup>-1</sup> have been reported [5], but in this case high purity carbonyl iron was used.

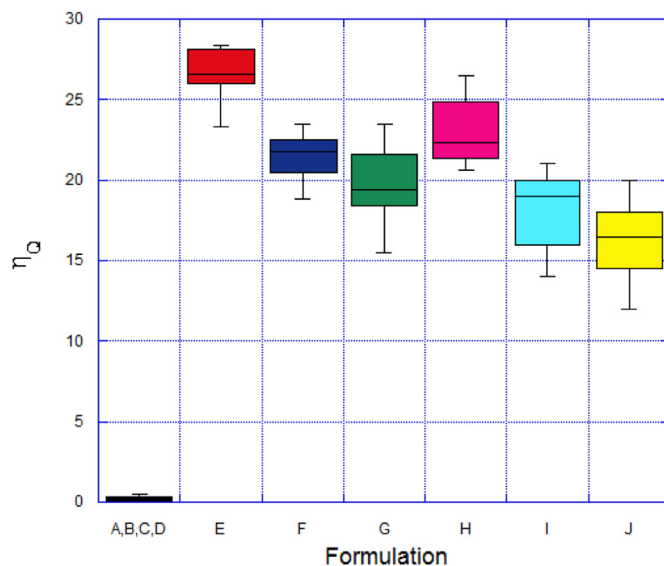
Although, Figs. 1 and 2 were made by considering samples that are reproducible (with the term “reproducible” we denote samples which do not deviate more than two standard deviations from the mean). Unfortunately, we have found a large variability between samples from the same formulation. So reproducibility is a major concern to develop the right electrode formulation; reasons for this variability include:

- Getting homogeneous electroactive pastes on electrodes of the same formulation (mixing problem)
- Iron electrodes tend to fall apart (to some extent) during the conditioning period
- It is difficult to apply the same amount of electroactive paste in the same area of the electrode

From that it follows that in order to perform a proper comparison between electrode formulations, we must consider all electrodes. Fig. 5 compares electrode formulations based on groups of 11 electrodes per formulation. Each group corresponds to a different box (except for formulations A to D which exhibit virtually zero coulombic efficiency); each line within the box represents the mean coulombic efficiency. The whiskers indicate extreme values for each formulation.

Fig. 5 reveals the use of either Bi<sub>2</sub>S<sub>3</sub> or FeS (formulations E and H respectively) will increase the coulombic efficiency of the NiFe cell. The addition of either metallic bismuth or potassium sulphide (which in solution renders the soluble bisulfide anion) on the aforementioned cells seems to have little or even no effect on the charge–discharge coulombic efficiency.

In situations where a visual inspection of a graph (such as Fig. 5) is not sufficient to determine whether meaningful differences exist between treatments or formulations, then post-hoc comparisons should be used. Although, in our case, some formulations are clearly different (for example formulations A and E), some others seem to be just slightly different (for example



**Fig. 5.** Comparison of NiFe cells produced with different additives (for the 30th cycle).

formulations F, G, H and I). Therefore, we shall use post-hoc comparisons to find meaningful differences between electrode formulations.

In order to conduct post-hoc comparisons between treatments (formulations in this case), it is mandatory to check whether or not our data is normally distributed. The Shapiro–Wilk test, a non-parametric test for normality, indicates there is no evidence against normality (all *p*-values are significant). This conclusion was corroborated by using the Kolmogorov–Smirnov test. The results can be found in Table 2.

Table 2 confirms that at the level of confidence  $\alpha = 0.05$ , there is no evidence against normality. Therefore, we can proceed with the analysis of variance.

Coulombic efficiency was explained by the factor treatment (type of additive used to produce each electrode). The analysis of variance reveals an *F* value of 787.6, which implies that the overall model is not only significant but there are also meaningful differences between treatments. The use of post-hoc comparisons (we shall use here the Tukey’s HSD) provide a means to find out where those differences exist.

The Tukey test reveals that the use of either elemental bismuth or potassium sulphide does not change the performance of the battery in an appreciable way. However, the combined use of both additives would decrease the performance of the battery in an appreciable manner. The authors believe this might be due to the fact that such formulations require less electroactive material (iron) present in the formulation, which drastically reduces the

**Table 2**  
Shapiro–Wilk (SW) and Kolmogorov–Smirnov (KS) tests of normality (*p*-values).

Additives	<i>P</i> <sub>SW</sub>	<i>P</i> <sub>KS</sub>
A	0.2685	0.0699
B	0.07834	0.4816
C	0.2883	0.1081
D	0.7629	0.1723
E	0.1934	0.4807
F	0.1485	0.4114
G	0.8858	0.3342
H	0.141	0.1953
I	0.07685	0.05793
J	0.892	0.6836



performance of the battery. By using the Tukey's HSD, we conclude the following groups of formulations produce NiFe cells with virtually the same coulombic efficiency:

- A, B, C, D
- F, G (but they are different to E)
- I, J (but they are different to H)

From the experimental results, it necessarily follows that metallic bismuth would not increase coulombic efficiency as has been suggested [5].

The analysis of variance and the post-hoc tests indicate that there are meaningful differences between formulations based on  $\text{Bi}_2\text{S}_3$  and FeS. It is clear that bismuth sulphide renders NiFe cells that outperform their iron sulphide counterparts. However, iron sulphide is by its own right a cost effective solution for improving NiFe cells.

The use of potassium sulphide has shown two things: first of all, the presence of the soluble bisulfide anion ( $\text{HS}^-$ ) is not sufficient to increase the coulombic efficiency of a NiFe cell; and second, sulphur (coming from  $\text{K}_2\text{S}$ ) cannot easily react with iron to form iron sulphide for otherwise, the electrodes prepared with  $\text{K}_2\text{S}$  would, in the long run, perform as if they were prepared with iron sulphide, so we would have noted an improvement in the coulombic efficiency, which never happened. By using the same line of thought, we concluded that the presence of metallic bismuth does not favour the reaction between sulphur and iron.

The fact that metallic bismuth seems to have little effect on improving the coulombic efficiency of a NiFe cell while iron sulphide is playing a major role on it, would suggest that micro-nucleus of FeS could be formed from bismuth sulphide. However, our XRD results suggest this is not the case and the reaction of iron with sulphur to produce FeS is unlikely at best. Fig. 6 confirms the presence of  $\alpha$ -Fe and  $\text{Fe}(\text{OH})_2$ ; as previously explained, functional groups of the form Fe–S were not detected.

Unfortunately, under our experimental conditions, we found no evidence of any reaction between potassium sulphide with either bismuth or bismuth sulphide, nor we found any type of synergistic effect between them that could explain the reactivity of the iron electrode under strong alkaline conditions, so more research is still needed.

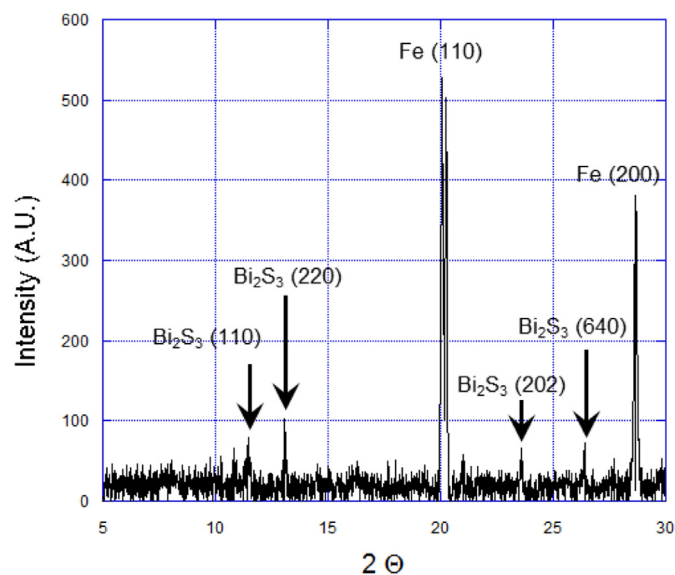


Fig. 6. XRD for a  $\text{Bi}_2\text{S}_3$  and  $\text{K}_2\text{S}$  containing electrode (sample G).

As a consequence, we believe bismuth sulphide should either be able to:

- decompose and react with iron, in such manner that complex Fe–S–Bi functional groups are formed
- play an active role in the passivation of the iron electrode
- modify the reactivity of the iron electrode (altering the Fermi level or by affecting the structure of the double layer)

When looking at the utilization of the electroactive material, we also found great variability, as when investigating coulombic efficiency of NiFe cells. We believe this is because during the first cycles of charge and discharge, part of the electroactive paste is dissolved, so the total amount of iron in the electrode decreases with the cycle number until the conditioning period is finished. Visual observation of the cells reveals that during the initial cycles of charge and discharge, as the iron electrode degrades, an iron rich precipitate forms. The degradation of the iron electrode means that with each piece of electrode that falls apart, new electroactive material would become available for the charge and discharge of the cell to proceed.

By proceeding in a similar way as when investigating the coulombic efficiency of our NiFe cells, we have found meaningful differences between formulations E and H (utilizations of 29 and 21% respectively). Therefore, we can conclude that bismuth sulphide outperformed iron sulphide as an additive in the production of NiFe cells.

Although, very large capacities (close to  $800 \text{ mAh g}^{-1}$ ) have been reported for nano-structured iron electrodes [4,10,11,15], we have achieved almost  $240 \text{ mAh g}^{-1}$ , which given the fact that we have used neither nano-size, nor ultra-pure reactants, can be considered as a major achievement.

In order to investigate the electrochemical properties of the electroactive paste used to produce the NiFe cells, cyclic voltammetry experiments were conducted under strong alkaline conditions (28.5% KOH). Each electrode formulation was investigated after conditioning (50 cycles of charge and discharge).

As shown in Fig. 7, two well resolved anodic peaks appearing from between  $-0.8$  and  $-0.6 \text{ V}$  (vs. SCE) and corresponding to the oxidation of Fe(0) to Fe(II) and Fe(II) to Fe(III) were identified. Likewise, a cathodic peak appearing near  $-0.9 \text{ V}$  (note the

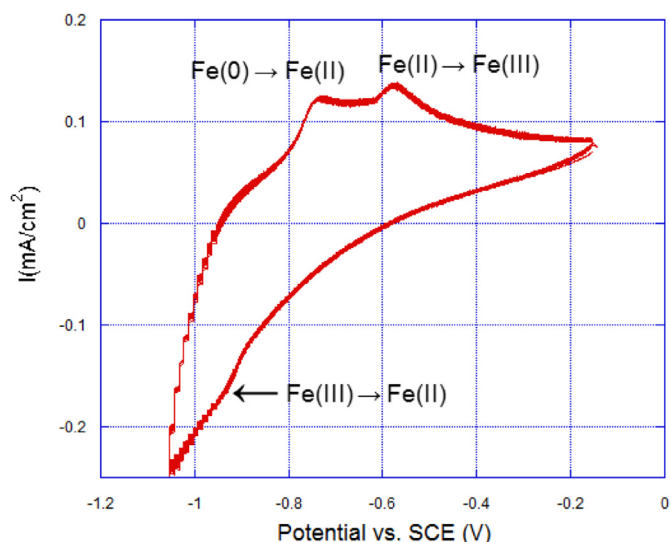


Fig. 7. Cyclic voltammetry of sample G in aqueous KOH 28.5% at a scan rate of  $0.5 \text{ mV s}^{-1}$ .

inflection point) was found and related to the reduction of Fe(III) to Fe(II). We couldn't detect the cathodic peak corresponding to the reduction of Fe(II) to Fe(0). Similar results were found for each iron electrode formulation listed in Table 1.

It has been suggested that one way in which iron sulphide could improve the NiFe cell coulombic efficiency is by preventing the oxidation of the iron electrode [16,17]. This observation confirms that passivation of the iron electrode is key to understand the evolution of hydrogen under strong alkaline conditions. In fact, it has been proposed that both bismuth sulphide and iron sulphide determine the passivation state of the iron electrode under alkaline conditions [8]. Our results are in line with these observations, but we can only conclude that either hydrogen evolution is determined by the passivation of the electrode or it is determined by the electronic properties of the iron electrode after using Bi<sub>2</sub>S<sub>3</sub> or FeS or a combination of both.

The phenomenon of passivation has been ascribed to the spontaneous formation of a surface oxide layer that prevents an electrode from corroding. However, the detailed mechanism is still poorly understood [18].

It is well known that hydrogen can enter into metals and alloys during electrochemical process. In aqueous media, the entry of hydrogen into transition metals such as iron or nickel is favoured by the presence of sulphur containing compounds [19,20]. Broadly speaking reduced sulphur species such as HS<sup>-</sup>, S<sup>2-</sup> and H<sub>2</sub>S are some of the most common promoters of hydrogen ingress into iron [20]. So we believe that the passivation of the iron electrode is strongly dependent upon its hydrogen content, for hydrogen promotes the reduction of Fe(III) to Fe(II), and the passive film on iron would consist on a structure that would resemble either a spinel (magnetite Fe<sub>3</sub>O<sub>4</sub>) or even a defective maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>); in general, other forms of iron could also be part of that film [21].

It has been reported that hydrogen evolution and ingress into iron is strongly enhanced by renewal of the metal surface [22]. Fig. 2 has shown that the performance of the iron electrode increases with the cycling number, until it reaches a plateau. We believe that the first cycles of charge and discharge are crucial for the final performance of the NiFe cell.

Finally, the authors believe that a synergistic effect between the presence of sulphur species (either FeS or Bi<sub>2</sub>S<sub>3</sub>) and the degradation of the iron electrode during the conditioning period could explain the reactivity of the iron electrode. This theory is supported by observations that have been made during the hydrogen evolution reaction under alkaline conditions [23].

#### 4. Conclusions and future work

By using a cost effective formulation, we have achieved NiFe cells that render coulombic efficiencies in the order of 30%. Likewise, the utilization of the electroactive material was in the order of 25% and the utilization of the capacity of the anode in the order of 240 mAh g<sup>-1</sup>. These results are very promising as we haven't used any ultra-pure reactant, nor we have nano-structured the electrode.

Bismuth sulphide increases coulombic efficiency on NiFe cells almost 30% more than iron sulphide. These aspects require further

confirmation by investigating iron sulphide and bismuth sulphide based formulations for iron electrodes.

Unlike bismuth sulphide, metallic bismuth has proven to be incapable to improve the performance of aqueous NiFe cells. Likewise, the presence of the soluble bisulfide anion (HS<sup>-</sup>) has no influence on the overall coulombic efficiency of the NiFe cell.

The data gathered during this investigation exhibits large variability; therefore, we had increased the number of replicates to increase the statistical force of the analysis. In addition, we have found no evidence against normality, nor we have found reasons to reject the validity of an ANOVA test. The differences between treatments were found by using post-hoc comparisons; in this case, we have used the Tukey HSD.

Our initial results indicate that NiFe cells produced with bismuth sulphide exhibit better performance than their iron sulphide based counterparts. We believe, however, that both additives (Bi<sub>2</sub>S<sub>3</sub> and FeS) would play a major role in the final development of a NiFe cell cost effective solution.

#### Acknowledgements

The authors would like to acknowledge the U.K. Engineering and Physical Sciences Research Council for supporting this work (EP/K000292/1; SPECIFIC Tranche 1: Buildings as Power Stations).

#### References

- [1] A. Chaurey, S. Deambi, *Renew. Energy* 2 (1992) 227–235.
- [2] G. Halpert, *J. Power Sources* 12 (1984) 177–192.
- [3] A.K. Shukla, S. Venugopalan, B. Hariprakash, *J. Power Sources* 100 (2001) 125–148.
- [4] H. Wang, Y. Liang, M. Gong, Y. Li, W. Chang, T. Mefford, J. Zhou, J. Wang, T. Regier, F. Wei, H. Dai, *Nat. Commun.* 3 (2012) 1–8.
- [5] A.K. Manohar, S. Malkhandi, B. Yang, C. Yang, G.K.S. Prakash, S.R. Narayanan, *J. Electrochem. Soc.* 159 (2012) A1209–A1214.
- [6] J.O. Gil Posada, P.J. Hall, *J. Power Sources* 262 (2014) 263–269.
- [7] R. Sabella, I. Paseka, *J. Appl. Electrochem.* 20 (1990) 500–505.
- [8] T.S. Balasubramanian, A.K. Shukla, *J. Power Sources* 41 (1993) 99–105.
- [9] K. Vijayamohanam, A.K. Shukla, S. Sathyanarayana, *J. Electroanal. Chem. Interfacial Electrochem.* 289 (1990) 55–68.
- [10] P. Periasamy, B. Ramesh Babu, S. Venkatakrishna Iyer, *J. Power Sources* 62 (1996) 9–14.
- [11] Z. Liu, S.W. Tay, X. Li, *Chem. Commun.* 47 (2011) 12473–12475.
- [12] A.K. Manohar, C. Yang, S. Malkhandi, B. Yang, G.K.S. Prakash, S.R. Narayanan, *J. Electrochem. Soc.* 159 (2012) A2148–A2155.
- [13] S. Malkhandi, B. Yang, A.K. Manohar, G.K.S. Prakash, S.R. Narayanan, *J. Electrochem. Soc.* 135 (2012) 347–353.
- [14] A.K. Manohar, C. Yang, S. Malkhandi, G.K.S. Prakash, S.R. Narayanan, *J. Electrochem. Soc.* 160 (2013) A2078–A2084.
- [15] M.K. Ravikumar, T.S. Balasubramanian, A.K. Shukla, *J. Power Sources* 56 (1995) 209–212.
- [16] M. Jayalakshmi, B. Nathira Begum, V.R. Chidambaram, R. Sabapathi, V.S. Muralidharan, *J. Power Sources* 39 (1992) 113–119.
- [17] M.E.G. Lyons, L.D. Burke, *J. Electroanal. Chem.* 170 (1984) 377–381.
- [18] I. Diez-Perez, F. Sanz, P. Gorostiza, *Electrochem. Commun.* 8 (2006) 1595–1602.
- [19] G. Williams, H.N. McMurray, R.C. Newman, *Electrochem. Commun.* 27 (2013) 144–147.
- [20] I. Flis-Kabulska, J. Flis, T. Zakroczymski, *Electrochim. Acta* 52 (2007) 7158–7165.
- [21] H.B. Shao, J.M. Wang, W.C. He, J.Q. Zhang, C.N. Cao, *Electrochem. Commun.* 7 (2005) 1429–1433.
- [22] I. Flis-Kabulska, *Electrochem. Commun.* 11 (2009) 54–56.
- [23] R. Solmaz, G. Kardaş, *Electrochim. Acta* 54 (2009) 3726–3734.