

## Original Research Article

## Surface response investigation of parameters in the development of FeS based iron electrodes



Jorge Omar Gil Posada\*, Peter J. Hall

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

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## ABSTRACT

In this article we use a surface response approach to investigate the effect of iron sulphide as well as the compositions of PTFE in the overall coulombic efficiency of a NiFe cell battery. Our results demonstrate that iron sulphide favours the process of charge/discharge of a NiFe cell. Our experimental results indicate iron sulphide improves the performance of a NiFe cell, but more research is still needed in order to achieve a large scale utilisation of such cells.

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## Introduction

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], and almost 16% of China by 2020 among others [2].

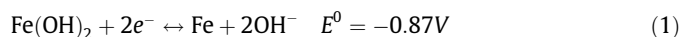
Wind power, one the world's fastest growing technologies of its kind [3], allows the conversion of wind energy into more useful forms of energy. As offshore wind is stronger than on land, offshore wind farms have the potential to convert larger amounts of wind energy into more useful forms of energy (such as electricity) than their onshore counterparts. However, wind energy is not always available on demand; energy experts have identified rechargeable aqueous batteries, such as lead-acid and nickel-iron, as suitable solutions to overcome this problem [4]. The reasons for this are many, but in general aqueous battery technology has the potential to provide an efficient, safe, environmentally friendly, and cost effective way of storing grid-scale amounts of energy, thus reducing the impact of wind forecast errors and also minimising the asynchronous problem of energy generation and demand.

Successfully commercialised in the early 20th century [5], nickel/iron (NiFe) batteries are aqueous rechargeable energy storage devices that fell out of favour with the advent of cheaper lead-acid cells. There has been a resurgence of interest in NiFe cells

arising from their environmentally friendliness, longevity, tolerance to electrical abuse (such as overcharge, over-discharge, being idle for extended periods and short-circuit conditions) and their potential to be a cost-effective energy storage solution for off-grid applications; in particular, NiFe cells are well suited for offshore energy storage. In general, NiFe cells are seen to be more cost-effective and environmentally friendly than their lead-acid counterparts. Unfortunately, these cells are limited by their relatively low energy and power densities; in addition, the charging efficiency of the iron electrode is drastically reduced by diverting part of the charging current in the wasteful evolution of hydrogen.

## Theory

The primary process taking place during the charging of an iron cell should be reduction of iron(II) to iron(0), as indicated by the forward reaction in Eq. (1); in the same way, the oxidation of iron(0) to iron(II) should take place during the discharging process of the electrode, as indicated by the backward reaction in Eq. (1) [6,7].



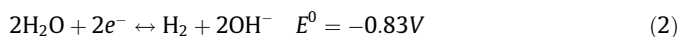
As has been described above, there are many reasons favouring the use of NiFe cells such as robustness, longevity, environmental friendliness and the relatively low cost of bulk raw materials. However, NiFe cells are limited by their relatively low energy and power densities. A further drawback is the relatively low efficiency of the charge–discharge cycle, with energy efficiencies of 50–60%

\* Corresponding author. Tel.: +44 0 114 222 8257; fax: +44 0 114 222 7501.

E-mail address: [j.o.gil-posada@sheffield.ac.uk](mailto:j.o.gil-posada@sheffield.ac.uk) (J.O.G. Posada).

being widely quoted [5,6]. The low energy efficiency can be attributed to the evolution of hydrogen as well as an unoptimised cell design.

It has been long recognised that under alkaline conditions (in the case of NiFe cells, close to 28.5% of KOH) water decomposes into hydrogen during the charging of an iron electrode; as a consequence, part of the charging current is wasted in producing hydrogen thus lowering the overall coulombic efficiency of the cell, as illustrated by Eq. (2).



Therefore, with the intention of improving the performance of the NiFe cell, many attempts have been made to develop iron based formulations that minimise the evolution of hydrogen under strong alkaline conditions. As a consequence; while some research projects focus on finding the conditions to maximise the evolution of hydrogen [8], we are interested in the reduction (or even in the total prevention) of this reaction. The hydrogen evolution reaction is currently studied in many applications such as modern electrochemical technology as well as in future energy conversion [9,10].

It has been proposed that the evolution of hydrogen under alkaline conditions is determined by the passivation of the iron electrode. This process can be understood as the spontaneous formation of a surface oxide layer that prevents the iron electrode from corroding. Unfortunately, this process is poorly understood [11].

In order to improve the performance of iron electrodes, scientists have investigated many sulphur containing additives, such as bismuth sulphide [12–14], thiourea [15], lead sulphide and iron sulphide [16], among others [17]. It has been reported that hydrogen can enter into transition metals such as iron during electrochemical process thus deteriorating its mechanical properties (hydrogen embrittlement). In any aqueous cells, this process is promoted by reduced sulphur species such as  $\text{HS}^-$ ,  $\text{S}^{2-}$  and  $\text{H}_2\text{S}$  [18,19]. In addition, it has been reported that hydrogen promotes the reduction of Fe(III) to Fe(II) so it also modifies the charge/discharge chemistry of the NiFe battery [18].

By considering what has been previously explained, we decided to investigate the potential of iron sulphide as a sulphur containing additive, in the development and improvement of NiFe cells.

## Experimental

Iron electrodes were produced by coating strips of nickel foam (40 mm × 10 mm × 1.8 mm) with an iron active paste which consists of varying amounts of iron powder (purity 99.5%, <10 μm, from Alfa Aesar) with PTFE (Teflon 30-N, 59.95% solids, from Alfa Aesar) and iron sulphide (purity 99.5%, from Alfa Aesar). Note that in this article, we denote the iron powder as the “electroactive material”.

In essence, electrodes were coated and then vacuum dried for at least 5 h until a targeted amount of electroactive material was loaded on each electrode; this coating process was repeated until approximately 0.2 g of iron powder were loaded on an area of approximately 1 cm<sup>2</sup>. More experimental details can be found in our previous publication [12].

Once produced, iron electrodes were tested in a three-electrode cell. Commercial nickel electrodes (obtained from a nickel–iron battery) were used as the counter electrodes. A concentrated solution of potassium hydroxide (28.5%) was used as the electrolyte. All potentials were measured against a mercury/mercury oxide (MMO) reference electrode ( $E_0^{\text{MMO}} = 0.098\text{ V vs. NHE}$ ). Experiments of charge and discharge were performed on a 64 channel Arbin SCTS 5 mA. An sketch of the cell test configuration can be found in Fig. 1.

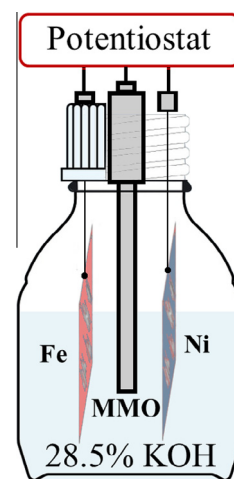


Fig. 1. Test cell configuration.

In order to efficiently investigate the composition effect of Fe, PTFE and FeS on cell performance, an experimental design based on Table 1 was proposed.

## Results and discussion

By considering Table 1 and using the mixing rules in a three dimensional concentration space, a simplex centroid design based on a conventional central composite design was proposed. A total of 11 different formulations (six replicates per formulation) were produced and tested; once that was done, a quadratic surface response was found by considering a second order Scheffé polynomial of the form:

$$\eta_Q = \lambda_1 Y_F + \lambda_2 Y_S + \lambda_3 Y_P + \lambda_4 Y_F Y_S + \lambda_5 Y_F Y_P + \lambda_6 Y_S Y_P \quad (3)$$

Where the term  $\eta_Q$  represents the coulombic efficiency, the  $Y$  terms represent the weight percent of each component and the subscripts  $F$ ,  $S$  and  $P$  correspond to iron, iron sulphide and PTFE respectively.

$$\eta_Q = -0.14374Y_F - 12.19605Y_S - 5.59371Y_P + 0.16534Y_F \times Y_S + 0.07393Y_F \times Y_P + 0.14282Y_S \times Y_P \quad (4)$$

Where any positive sign in front of each composition term indicates a synergistic effect; in the same way, any negative sign indicates an antagonistic effect. The ANOVA test reveals that at the level of confidence  $\alpha = 0.05$  all parameters of the model are significant.

Fig. 2 provides a three dimensional representation of Eq. (4). Note that we have plotted the coulombic efficiency ( $\eta_Q$ ) in logarithmic coordinates; in addition, the concentrations of iron sulphide, PTFE and iron are denoted by FeS, PTFE and Fe respectively. For the sake of clarity, we have highlighted in red colour the regions where coulombic efficiency is maximised; likewise, we have used blue to denote formulations that minimise coulombic efficiency and yellow for intermediate values of the same parameter. Finally, the contour curves represent formulations that render cells of the same coulombic efficiency.

Table 1  
Experimental definition of factors and levels (concentrations in weight percent).

Factor	Low (%)	High (%)
FeS	2	20
PTFE	4	15
Fe	65	84

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