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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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ABSTRACT

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/Bi₂S₃ 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:

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

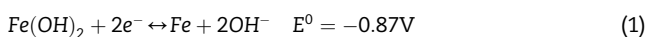
These aspects will increase the price of the battery and would polarize general opinion against large scale implementation of the intended solution.

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.

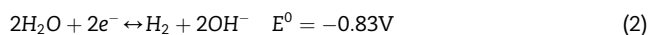
There are, of course, many challenges preventing a large scale utilization of NiFe cells for offshore wind applications, such as low cell efficiency, electrolyte decomposition (hydrogen evolution), and low energy and power densities [31,32]. Essentially, the major challenge preventing this technology 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 (Fe²⁺) to metallic iron (Fe⁰); 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].



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).



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 Bi₂S₃. 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 cm². 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

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