An aqueous alkaline battery consisting of inexpensive all-iron redox chemistries for large-scale energy storage

L. Wei¹, M.C. Wu¹, T.S. Zhao*, Y.K. Zeng, Y.X. Ren

HKUST Energy Institute, Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

HIGHLIGHTS

- Investigate the performance of a novel all iron-based alkaline battery.
- The coulombic efficiency reaches 99% at current density higher than 4 mA cm⁻².
- The energy efficiency maintained above 76% at 2 mA cm⁻² over 150 cycles.
- The battery achieves a significantly low active material cost of $22 kW h⁻¹.

GRAPHICAL ABSTRACT

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ABSTRACT

In this work, an iron-based alkaline battery using the same redox-active element featuring different coordination chemistries is developed and tested. The battery achieves a significantly low active material cost per kilowatt hour ($22 kW h⁻¹) due to the inherently inexpensive price and availability of iron oxide and iron ferricyanide, particularly when compared with state-of-the-art vanadium redox flow batteries ($118 kW h⁻¹) or the commercialized nickel cadmium battery ($51 kW h⁻¹). Experimental results show that the present battery creates an equilibrium cell potential of 1.2 V and its coulombic efficiency reaches as high as 99% at a current density higher than 4 mA cm⁻². Moreover, the energy efficiency can be maintained above 76% and the capacity decay rate is only 0.15% per cycle at a current density of 2 mA cm⁻² over 150 cycles. With these advantages, the battery offers a promising solution for low-cost energy storage applications.

1. Introduction

The increasing utilization of renewable energies such as solar and wind requires energy storage systems to bridge supply shortfall. Up to now, various technologies have been developed, including physical method such as compressed air and pumped hydro, and electrochemical method such as rechargeable batteries and regenerative fuel cells [1–4]. Among these advanced energy storage technologies, rechargeable batteries which capitalize on two redox reactions to perform the reversible conversion between electrical energy and chemical energy are regarded as one of the most promising candidates and have been attracted much attention due to their high energy efficiencies, flexible design and relatively low construction cost [5–8]. In the past decades, although considerations of many elements in various redox couples have been

* Corresponding author.

E-mail address: metzhao@ust.hk (T.S. Zhao).

¹ These authors contributed equally to this work.

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proposed to constitute new batteries, a majority of their commercialization is hindered by both technical and economic barriers. Aiming to this situation, the search for novel electrochemical redox species based on inexpensive components, with high redox potential, and exhibiting fast electrode kinetics is needed for industry acceptance and widespread implementation of this technology [9–11].

Out of various organic-inorganic batteries, the aqueous batteries consisting of soluble redox pairs separated by ion-exchange membranes, are particularly suitable for large-scale energy storage due to the inherent safety and scalability. Unfortunately, the imperfect ionic selectivity of existing ion exchange membranes inevitably leads to undesired crossover of redox species between negative and positive electrolytes. The crossover phenomenon, which is well known as electrolyte contamination, can cause permanent capacity losses and simultaneously lower the operating coulombic efficiency (CE), threatening the reliability and durability of batteries. An effective approach to alleviate this problem is to use the same redox-active element to create the two-redox species. One representative example is all-vanadium redox battery [12]. However, low earth abundance, high cost and volatile price limit its widespread commercial adoption. Apart from this example, several other batteries based on the same redox-active reactants with different valence states have also been proposed, including all-copper [13,14], all-iron (all-Fe) [15–17], all-lead [18], and all-chromium batteries [19]. In particular, the all-Fe batteries have some outstanding advantages such as low chemical toxicity and very low material cost since iron element is environmentally friendly and very abundant in the earth. Existing all-Fe batteries were proposed by Hruska et al. and Gong. et al., respectively [16,17]. Both of them are great inventions.

However, hydrogen evolution reaction (HER) as a side reaction poses a serious challenge in the battery pioneered by Hruska because the standard redox potential of Fe2+/Fe is 450 mV more negative than that of HER at pH = 0. Moreover, Gong et al. used expensive organic TEOA ligands coordinating with metal ions to form soluble redox pairs in the negative electrolyte, which increases the cost of the electrolyte to some extent.

Herein, we investigated another type of all-Fe battery applying solid iron oxide and soluble iron ferricyanide as negative and positive redox species. Although both iron oxide and iron ferricyanide are notable for their low cost and ubiquitous availability [20,21], the combination has not been reported in an open literature. Different from conventional acid and neutral batteries, the present battery works in basic conditions by employing KOH as the supporting electrolyte. During operation, K+ and OH− migrate through the membrane to form a complete electric circuit. Though the alkaline electrolyte usually has a lower conductance (maximum value: 410 mS cm−1 for 4.6 M KOH at 25 °C) compared with acidic ones (maximum value: 825 mS cm−1 for 3 M H2SO4 at 25 °C), it tends to be less corrosive to the cell components, which translates to lower operation and maintenance costs [22]. Moreover, it may also alleviate the occurrence of undesired side reactions during battery cycling in acidic conditions (evolution of H2 and Cl2 gases) [23].

The negative iron electrode (Fe3O4/Fe) is demonstrated to have a long lifetime and does not form dendrites during operation since the electrodeposition process [20]. The main challenge in producing a suitable iron (Fe3O4/Fe) electrode for the iron-based batteries is to make more of the solid electrode accessible to the electrolyte by using nanostructured iron oxide to increase the surface area [24]. Other iron electrodes have demonstrated even greater utilization and performance when iron oxide nanoparticles supported on conductive carbon particles were used [25]. The positive ferri/ferrocyanide couple is commonly used as an electrochemical standard redox pair due to its well-defined redox behavior and fast electron transfer kinetics [26]. Its kinetics are even faster than the Fe3+/Fe2+ redox pairs and can drastically reduce the electrode overpotential during operation [16].

To evaluate the battery performance, a series of electrochemical properties of the redox couples and the charge/discharge cycling performance were investigated in this work.

The detailed working principle of the battery is illustrated in Fig. 1. Taken charge process as an example, Fe3O4 is reduced to metal iron at the negative electrode, while at the positive electrode, Fe(CN)63− is oxidized to form Fe(CN)64−. During discharge, reverse process occurs. The electrochemical process can be summarized as:

- at negative electrode:
  \[
  \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O} + 2\text{e}^- \leftrightarrow 3\text{Fe(OH)}_2 + 2\text{OH}^- \quad E^\circ = -0.88 \text{ V vs. SHE}
  \]

- at positive electrode:
  \[
  \text{Fe(CN)}_6^{4−} \rightarrow 2\text{e}^- \leftrightarrow \text{Fe(CN)}_6^{3−} \quad E^\circ = 0.36 \text{ V vs. SHE}
  \]

2. Experimental

2.1. Electrode preparation and battery assembly

Commercially available magnetite (Fe3O4, Aladdin) nanoparticles were used as the beginning material, which was at the discharged state. Fe3O4 carbon black (8.96 m2 g−1, Aladdin) and PTFE emulsion (5 wt%, Dupont, USA) at the mass ratio of 8:1 were firstly mixed in absolute ethanol and ultrasonically stirred for 1 h. The slurry was then pasted uniformly onto a nickel foam and dried in air at 100 °C overnight, reaching a loading of 6 mg cm−2. The obtained electrode is thereafter denoted as Fe3O4/C/nickel (purity 99.8%, porosity 97.2%, 1 mm, average diameter of pores 200–600 µm, Shenzhen Poxon Machinery Technology Co., Ltd.). Before use, the nickel foam was treated with acetone, HCl and deionized water, each for 15 min, to remove the residues. The obtained electrode (active area 0.785 cm2) was used as the negative electrode. Commercially available graphite felt (SGL company, GFA series) with an uncompressed thickness of 3 mm was used as positive electrode. To avoid the crossover of ferri-cyanide ions, 0.4 mL electrolyte prepared by dissolving 0.2 M K4Fe(CN)6 in 3 M KOH aqueous solution was added in both positive and negative side, respectively. Nafion 212 (thickness: 50 µm, Dupont, USA) was employed as the membrane. The Nafion membrane was immersed into 3 M KOH solutions for 3 days at room temperature to

Fig. 1. Schematic of the battery during charge process.
exchange the K+ with H+ on the sulfonic functional groups before use. The performance of the battery was tested in a home-made static setup (see Fig. S1).

2.2. Material characterizations

Transmission electron microscopy (TEM) images of Fe3O4 nanoparticles were identified with a high-resolution JEOL 2010F TEM system with a LaB6 lamp at 200 kV. The electrode morphologies were analyzed by scanning electron microscope (JEOL 6700F), and the elemental contents were determined by an energy dispersive X-ray spectroscopy (EDX) mapping. The crystal phase and composition of the nanowires were analyzed by a Philips high-resolution X-ray diffraction system (XRD, model PW 1825) using a Cu Ka source operating at 40 keV.

2.3. Electrochemical measurement

The electrochemical performance of the Fe(CN)6^{3−}/Fe(CN)6^{4−} redox species was investigated by cyclic voltammetry (CV) via a typical three-electrode system. A glassy carbon electrode (GCE) (5 mm in diameter) served as the working electrode, while a saturated calomel electrode (SCE) assembled in a KCl salt bridge and platinum mesh were employed as reference and counter electrode, respectively. For the Fe3O4/Fe side, the same GCE coated with Fe3O4 active materials (30 μL of the above-mentioned slurry was pipetted on top of GCE and dried in air) was served as working electrode. The electrolyte used for CV tests in the Fe3O4/Fe side is 3 M KOH while the one in the Fe(CN)6^{3−}/Fe(CN)6^{4−} side is 0.2 M K4Fe(CN)6 in 3 M KOH solution. The recorded CV curves were obtained using a potentiostat (EG&G Princeton, model 2273) at room temperature. The battery performance was assessed in a battery test system (BT2000, Arbin Instrument, Inc.).

Fig. 2. (a) Typical TEM image of Fe3O4 nanoparticles. (b) XRD pattern of original and Fe3O4 decorated nickel foam. (c) SEM image of Fe3O4 decorating on the surface of nickel foam fibers. (d) Elemental mapping of the same region, indicating spatial distribution of Ni (blue), Fe (red), O (green), and C (yellow), respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

The typical TEM image of Fe3O4 nanoparticles is shown in Fig. 2a. The average particle size of the Fe3O4 nanoparticles is about 20 nm and they are usually aggregated to form a cluster due to their magnetic property. Fig. 2b shows the XRD patterns of the as-prepared Fe3O4/C/nickel foam electrode. For the original nickel substrate, three strong peaks depict at 44.5°, 51.8° and 76.4°, namely, reflecting the planes (1 1 1), (2 0 0) and (2 2 0) of face-centered cubic nickel (JCPDS No. 04-0850). For the Fe3O4 deposited nickel electrode, in addition to the peaks corresponding nickel, four new peaks located at 30.10°, 35.54°, 56.98° and 62.57° are clearly observed, which are ascribed to the crystal planes of (2 2 0), (4 2 2), (5 1 1) and (4 4 0) of Fe3O4 (JCPDS No. 04-0850) respectively, suggesting the Fe3O4 was successfully decorated. The distribution of the Fe3O4 on the fiber of nickel foam was further revealed by SEM (Fig. 2c) and EDX mapping (See Figs. 2d and S2). It is clearly observed that iron and oxygen elements are well distributed across the mapping section, indicating the relatively uniform dispersion of Fe3O4.

The electrochemical behaviors of the redox couples were studied by cyclic voltammetry (CV) and the results are shown in Fig. 3. Fig. 3a presents the CV results at a scan rate of 30 mV s⁻¹. It predicts the formal-potential difference between the two redox pairs approaching 1.2 V, which is in well agreement with the theoretical calculation. The battery voltage is lower than zinc-nickel and all vanadium battery, however, it keeps the same or even exceeds some other kinds of typical rechargeable batteries (see Fig. 3b) [26–29]. It is also worth noting that although the standard potential of the Fe(CN)6^{3−}/Fe(CN)6^{4−} is reported to be 0.12 V versus SCE, the formal potential depends on the ionic strength of the solution and can reach around 0.25 V with an ionic strength effect [30]. In terms of separate regions, the Fe(CN)6^{3−}/Fe(CN)6^{4−} redox pair is composed of two kinds of anions and can be easily captured. As for the Fe3O4/Fe couple, two oxidation peaks are observed at −1.0 and −0.7 V, which may be ascribed to the oxidation
of Fe to Fe(OH)$_2$ and Fe(OH)$_2$ to Fe$_3$O$_4$ [31], respectively. However, when reversely scanned, only one reduction peak appears, possibly due to the reaction peaks merged as one peak [32]. Although HER was reported to be an issue in rechargeable Fe-air batteries, no HER peak was detected even when the negative electrode potential reached $-1.3$ V, indicating that HER is not severe in the negative electrode [33]. Meanwhile, calculated from the oxidation and reduction peak separation (0.09 V for Fe(CN)$_6^{3-/4-}$ and 0.48 V for Fe$_3$O$_4$/Fe), it is obvious that the reversibility of Fe(CN)$_6^{3-/4-}$ couple is much better than that of the Fe$_3$O$_4$/Fe. The excellent reversibility of Fe(CN)$_6^{3-/4-}$ couple in alkaline solution has also been proven by other groups [21], suggesting it a very promising redox couple for rechargeable batteries. In addition to the reversibility and the redox potential, the stability is also of great significance. Therefore, repetitive CVs were performed (100 scans at 30 mV s$^{-1}$) and the results are shown in Fig. 3c and d. The peak currents of the Fe$_3$O$_4$/Fe redox couple exhibit slight increase with cycle number rising due to the electrode wettability to aqueous electrolyte gradually becomes better. Both redox couples exhibit good repeatability without significant degradation and the value of the anodic peak current/cathodic peak potential remains essentially the same throughout the entire test process, which can be perceived as a first indication of the electrode stability. The results are also in agreement with the previous literature reported about the stability of the electrodes [16,34]. Fig. 3e and f display the CV curves at different scan rates, upon increasing the scan rate, the anodic and cathodic peak current densities increase accordingly. The results indicate that the anodic and cathodic peak position of Fe$_3$O$_4$/Fe redox shifts more positively and negatively, which suggests that this redox reaction is quasi-reversible. While for the ferricyanide redox couple, the scan rate has minor effect on the peak voltage position, which again,
indicates its excellent reversibility.

To demonstrate the practical application of the battery, its performance was further studied by typical charge-discharge measurement. Fig. 4a shows the rate performance of the battery at current densities of 2, 4 and 6 mA cm$^{-2}$ with a cut-off voltage of 1.4 and 0.2 V for charge and discharge. The battery was run for 5 cycles at each current density. It is clearly demonstrated that the battery is capable of operating at different current densities without degradation. The average charge platform increases while the discharge platform decreases from 2 to 6 mA cm$^{-2}$ (see Fig. 4b), indicating that battery polarization increases quickly with operating current density. The corresponding C-rate performance is depicted in Fig. S3. There are two reasons responsible for this phenomenon: First, the activation loss is mainly caused by sluggish kinetics of Fe$_3$O$_4$/Fe redox reaction. Second, in the static setup, the distance between positive and negative electrode is more than 10 mm, inducing a high ohmic loss (3.52 $\Omega$ cm$^2$) at elevated current densities. Fig. 4c summarizes the coulombic and energy efficiency as well as the discharge capacity obtained at different densities. The energy efficiency and discharge capacity can reach 77% and 0.65 mA h cm$^{-2}$ at 2 mA cm$^{-2}$, respectively. Although the values quickly drop to 56% and 0.56 mA h cm$^{-2}$ at 6 mA cm$^{-2}$ due to above-mentioned battery polarization, the coulombic efficiency of battery keeps above 95% (at 2 mA cm$^{-2}$) and the battery did not show any coulombic efficiency loss. Notably, to assess the stability of the battery, we swiftly changed the operating current from 6 to 2 mA cm$^{-2}$ at the sixteenth cycle and noted that the efficiency and capacity is fully recovered, indicating the chemical robustness of the battery components in the alkaline solutions. Since the PMMA electrolyte tank is transparent, if HER occurs to form H$_2$ bubbles during battery operation, the H$_2$ bubbles will grow and attach on the electrode surface, which can be observed by reflection of liquid-gas interface [37]. The volume of the negative electrolyte will also decrease due to water splitting. However, no gas bubbles were observed and the liquid electrolyte level did not reduce during battery tests. Thus, we believe HER has little effect on battery operation.

The battery’s cyclic stability is of critical importance for practical applications. To further identify the stability and suitability of the components during battery operation, cycling tests were conducted at a current density of 2 mA cm$^{-2}$. The charge-discharge profiles of 150 cycles (115 h) are recorded (see Figs. 5a, 5b depicts the details of the 60–70th cycles), while the profiles for several selected cycles (1st, 30th, 60th, 90th, 120th and 150th cycles) are shown in Fig. 5a. From the cycle tests, it observed that the charge and discharge curves remain slight change with the increase of cycle number, which suggests that the present battery can sustain a good cycling performance. This is also
verified by the stable coulombic and energy efficiencies during cycling test, as shown in Fig. 5b. The energy efficiency kept above 76% without any observable decay, the slight variation may be ascribed to the room temperature difference day and night. To satisfy the grid storage requirement set by the U.S. Department of Energy (DOE), the system efficiency should be over 75% and 80% to meet the near-term and long-term target, respectively. The present system exhibits an energy efficiency of 76%, which can meet the near-term requirement. It is comparable to other aqueous batteries presented in Fig. 6. However, the efficiency as well as operating current density should be further enhanced to meet the long-term requirement. The capacity decay rate of the all iron alkaline battery in these 150 cycles is calculated to be only 0.15% per cycle (Fig. 5c), equaling to apparently higher capacity retention compared to other kind of acid-based batteries. These results further demonstrate the excellent stability of the battery over repeated cycling.

The cost of active species has been identified to be a crucial factor in determining the widespread deployment of the battery. One notable example is the vanadium redox battery, of which the further market penetration has been hindered by the high cost of the system, especially the vanadium-contained electrolyte. Thus, developing batteries with low-cost materials will be very attractive. Fig. 6 compares the cost of active materials used in this all iron battery with the well-known vanadium redox battery and other typical alkaline batteries according to a recent cost analysis model [35]. The cost can be calculated by the following equation:

$$C = \frac{3600}{EF} \sum_i \frac{Q M_i}{n_i}$$

where $C$ is the redox material cost per kilowatt-hour ($\$ \text{kWh}^{-1}$); $Q$ is the unit cost of the redox material ($\$ \text{kg}^{-1}$); $M$ is the molecular mass of the redox material (g mol$^{-1}$), respectively; $E$ is the standard cell voltage (V); $F$ is Faraday’s constant (96,485 C mol$^{-1}$). $n$ is the number of electrons involved in the redox reaction. The bulk prices of potassium ferrocyanide and iron oxide revolve around $6 and $2 per kilogram [26], respectively, leading to the total raw material cost of about $22 kW h^{-1}$ for the present system. This number is only about one fifth of the vanadium redox battery and other typical alkaline batteries such as polysulphide-iodine ($86 kW h^{-1}$) and commercialized nickel-cadmium battery ($51 kW h^{-1}$) [29,38]. Although the cost is slightly higher than that of zinc-nickel battery ($21 kW h^{-1}$), it is believed that the use of less-dendritic iron anode as well as the highly reversible Fe(CN)$_6^{3-}$/Fe (CN)$_6^{4-}$ cathode will extend the battery life and therefore, makes it competitive to other alkaline batteries. Moreover, the redox potential of the Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ redox couple is relatively low and involves no
strongly oxidative redox materials. Thus, inexpensive cell part materials and hydrocarbon membranes are expected to be suitable for the system, leading to the system more beneficial for large-scale energy storage system. Despite good stability and low active material cost, the most notable challenges confined the battery application are its high polarization resistance, which can be defined as low operating power density. Another challenge is the low utilization of the negative active species. The theoretical energy density of this system is 79 Wh kg$^{-1}$. However, due to the low utilization of the negative active species (30–40%) and relatively high activation loss, the practical energy density of the battery can only reach 25 Wh kg$^{-1}$. Although the preparation method is capable of uniformly distributing these particles on the nickel substrate from the EDS map shown in Figs. 2d and S2, the homogeneity is not perfect. Some magnetic Fe$_3$O$_4$ nanoparticles will still aggregate during electrode preparation process, lowering the utilization efficiency of active species. One effective strategy to improve utilization efficiency and reduce the high polarization resistance caused by anode is to make more surface of the solid electrode accessible to the electrolyte by using nano-sized particles or tubes of iron oxide embraced conductive carbon to increase the effective surface area and homogeneity in future work. Besides, further optimization of the battery structure, electrode treatment methods and selection of inexpensive membranes, which can be referenced from other electrochemical systems [39–42], will be helpful to improve the mass transfer of active species and simultaneously decreasing the ohmic loss of this battery. It is thus believed that developing electrodes and optimization of battery structures will further improve the efficiency, power density, energy density and cycling stability of the system.

4. Conclusions
In summary, we investigated an iron-based alkaline battery by combining Fe$_2$O$_3$/Fe and Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ in a single static cell configuration. The battery exhibited an equilibrium cell potential of 1.2 V, which is comparable to the existing batteries in the aqueous system. Experimental results showed that its coulombic efficiency reached as high as 99% at a current density higher than 4 mA cm$^{-2}$. The energy efficiency could be maintained at above 76% and the capacity decay rate was only 0.15% per cycle at a current density of 2 mA cm$^{-2}$ during cycle tests. Most importantly, the cost of active materials in the battery is significantly low due to their ubiquitous availability, compared with that of the state-of-the-art vanadium redox flow battery and the commercialized nickel cadmium battery. Future work involving increasing the sluggish kinetics of Fe$_2$O$_3$/Fe redox species and optimization of battery structure will further enhance the battery performance. With its inherent low material cost and large space for performance improvement, the battery possesses potential for the large-scale energy storage systems based on the DOE’s cost and performance requirements.

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Appendix A. Supplementary material
Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apenergy.2018.01.080.

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