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

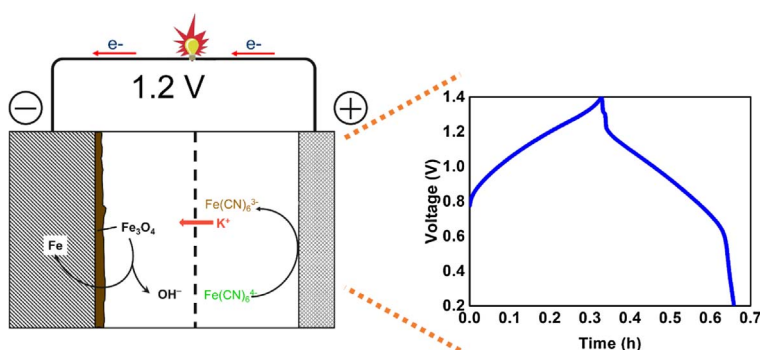L. Wei[1], M.C. Wu[1], T.S. Zhao[*], Y.K. Zeng, Y.X. Ren

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 $4\,\mathrm{mA\,cm^{-2}}$.
- The energy efficiency maintained above 76% at $2\,\mathrm{mA\,cm^{-2}}$ over 150 cycles.
- The battery achieves a significantly low active material cost of $22\,\mathrm{kW\,h^{-1}}$.

GRAPHICAL ABSTRACT

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 ($22\,\mathrm{kW\,h^{-1}}$) 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 ($118\,\mathrm{kW\,h^{-1}}$) or the commercialized nickel cadmium battery ($51\,\mathrm{kW\,h^{-1}}$). 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 $4\,\mathrm{mA\,cm^{-2}}$. 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 $2\,\mathrm{mA\,cm^{-2}}$ 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

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 Fe^{2+}/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 H_2SO_4 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 H_2 and Cl_2 gases) [23]. The negative iron electrode (Fe_3O_4/Fe) is demonstrated to have a long lifetime and does not form dendrites during operation since the electrochemical reactions do not involve solid-phase transformations of metal electrodeposition process [20]. The main challenge in producing a suitable iron (Fe_3O_4/Fe) electrode for the iron-based batteries is to increase the activity of the redox reactions and utilization of iron material. To address this issue, varieties of methods have been proposed 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 Fe^{3+}/Fe^{2+} redox pairs and can drastically reduce the electrode overpotential during operation [16]. To
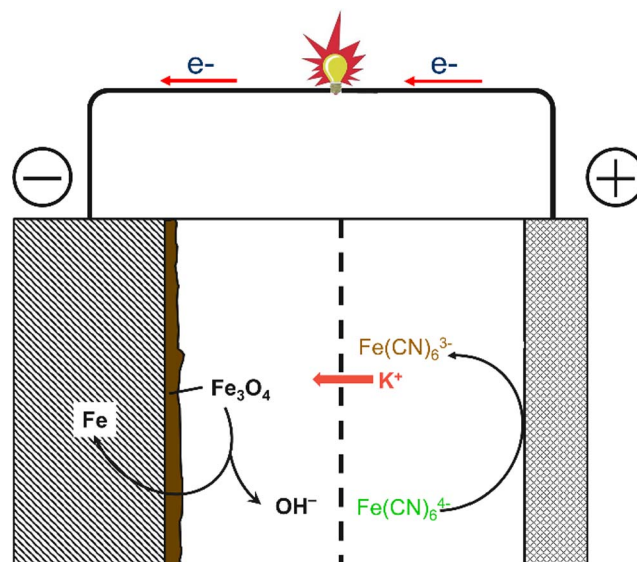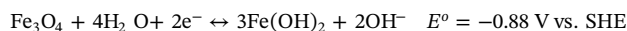

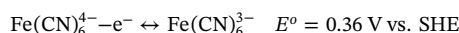**Fig. 1.** Schematic of the battery during charge process.

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, Fe_3O_4 is reduced to metal iron at the negative electrode, while at the positive electrode, $Fe(CN)_6^{4-}$ is oxidized to form $Fe(CN)_6^{3-}$. During discharge, reverse process occurs. The electrochemical process can be summarized as;

at negative electrode:

$$Fe_3O_4 + 4H_2O + 2e^- \leftrightarrow 3Fe(OH)_2 + 2OH^- \quad E^o = -0.88 \text{ V vs. SHE}$$

$$Fe(OH)_2 + 2e^- \leftrightarrow Fe + 2OH^- \quad E_o = -0.76 \text{ V vs. SHE}$$

at positive electrode:

$$Fe(CN)_6^{4-} - e^- \leftrightarrow Fe(CN)_6^{3-} \quad E^o = 0.36 \text{ V vs. SHE}$$

2. Experimental

2.1. Electrode preparation and battery assembly

Commercially available magnetite (Fe_3O_4, Aladdin) nanoparticles were used as the beginning material, which was at the discharged state. Fe_3O_4, carbon black (8.96 m^2 g^{-1}, Aladdin) and PTFE emulsion (5 wt%, Dupont, USA) at the mass ratio of 8:1:1 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 Fe_3O_4/C/nickel (purity 99.8%, porosity 97.2%, thickness 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 cm^2) 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 ferricyanide ions, 0.4 mL electrolyte prepared by dissolving 0.2 M K_4Fe(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