



# The effect of Na<sub>2</sub>S additive in alkaline electrolyte on improved performances of Fe-based air batteries



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## ABSTRACT

Fe-based air alkaline batteries are promising candidates for large scale energy storage due to their low cost, eco-friendliness and high energy density. In this work, pure iron was studied as negative electrode of Fe-air batteries with and without Na<sub>2</sub>S added to the KOH alkaline electrolyte in order to bring new insight on the mechanisms of inhibition of the hydrogen evolution reaction (HER) and improvement of the electrochemical performances of the Fe electrode. Electrochemical (CV, galvanostatic discharge), spectroscopic (XPS, ToF-SIMS) and microscopic (SEM) analysis were applied to characterize the effect of the sulfide additive (Na<sub>2</sub>S) on the electrochemical behavior of Fe electrodes and their chemical and morphological modifications. Surface analysis performed by XPS and ToF-SIMS revealed the formation of a markedly thicker oxide/hydroxide layer. The mechanism of formation of this thick oxide/hydroxide layer is initiated by the adsorption of sulfur (S<sub>ads</sub>) at the oxide/metal interface that inhibits the HER during the first stages of electrochemical process and promotes subsequent anodic oxidation. With the Na<sub>2</sub>S electrolyte additive, Fe(0)/Fe(II) conversion/deconversion is suppressed and charge/discharge proceeds mostly by Fe(II)/Fe(III) conversion/deconversion with improved capacity owing to the porous morphology of the oxide/hydroxide layer.

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## 1. Introduction

Rechargeable metal-air batteries represent a class of promising power sources for applications in next-generation electronics, electrified transportation and energy storage of smart grids, due to the remarkably high theoretical specific energy output (1.2, 1.3, 6.8, 8.1 and 13 kWh kg<sup>-1</sup> for Fe-, Zn-, Mg-, Al- and Li-air batteries, respectively, in aqueous electrolytes calculated on the basis of metal electrode) [1,2]. Among several types of metal-air batteries, Fe-air batteries have received considerable attention due to their high theoretical capacity, high electrochemical stability, low cost, and environmental safety [1–13]. However, the use of iron anodes suffers from a number of problems including hydrogen evolution

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and surface passivation by non-reducible surface oxide films. Hydrogen evolution is the most significant obstacle to the practical application of iron electrodes in alkaline aqueous solutions. The potentials of the Fe/Fe(OH)<sub>2</sub> reduction reaction and H<sub>2</sub>/H<sub>2</sub>O hydrogen evolution reaction are very close [14,15], and the hydrogen overpotential on iron surfaces is low, which limits its application in commercial batteries [16]. Sulfide salts are used as additives to improve its performance. Previous studies showed that the addition of either FeS, Bi, BiS, K<sub>2</sub>S to the iron electrodes [17–19] or Na<sub>2</sub>S, K<sub>2</sub>S to the KOH electrolytic solution [20–23] can significantly inhibit the HER. Some other recent studies show also inhibiting effect of organo-sulfur molecules on HER on iron-based electrodes [24]. However, these studies did not clarify the reaction mechanisms and the electrode surface modifications, through which, the additives suppressed the hydrogen evolution and enhanced the battery performance. In particular, no detailed surface analysis of the negative electrode modifications upon charge/discharge in the electrolyte with sulphide additives was reported.

In this work, we combine electrochemical characterization by cyclic voltammetry (CV) and galvanostatic discharge with surface

analysis by X-ray Photoelectron Spectroscopy (XPS), Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and Secondary Electron Microscopy (SEM) in order to bring deeper insight on how the HER is inhibited and the electrochemical performances of Fe electrode are improved. A model pure iron foil electrode was used as negative electrode in aqueous electrolyte of 6 M KOH without and with 0.01 M Na<sub>2</sub>S additive. The application of a model iron electrode can allow to better distinguish each single step of the reaction mechanisms and facilitates the surface analysis by the spectroscopic techniques employed in this work. The choice of the sulfide concentration was based on the results obtained by Hang et al. [17] showing a very significant effect on the suppression of HER even for this low quantity of sulfides in alkaline electrolyte. Na<sub>2</sub>S was used instead of K<sub>2</sub>S to avoid the possible interference of potassium from the electrolyte. The reaction mechanisms and electrode surface modifications through which the additive leads to better electrochemical performances are discussed.

## 2. Experimental

Iron electrodes in a form of discs (Ø 12 mm) were prepared from pure iron foils (Goodfellow, purity: 99.5 wt%; thickness: 0.05 mm). The iron electrode surfaces were prepared by mechanical polishing with diamond spray down to 1/4 µm and then successively rinsed in ultrasonic baths of acetone, ethanol, and ultrapure Millipore® water (resistivity > 18 MΩ cm) for 2 min each and dried in a flow of filtered compressed air.

The electrochemical measurements (CV and galvanostatic discharge) were performed in a three-electrode glass cell with an iron foil disc as the working electrode, platinum wire as the counter electrode and Hg/HgO in 1 M NaOH as the reference electrode. All potentials hereafter are given with respect to Hg/Hg<sup>+</sup> electrode. The cell was operated at room temperature in ambient air using an AutoLab (AUT30) electrochemical workstation. The working electrode area was delimited to 0.5 cm<sup>2</sup> by a viton O-ring. The electrolyte was 6 M KOH (Sigma-Aldrich, reagent grade) in ultrapure Millipore® H<sub>2</sub>O without or with 0.01 mol/L Na<sub>2</sub>S (Sigma-Aldrich, ACS reagent) additive. Cyclic voltammograms were acquired over a potential range of –1.3 to –0.1 V at a scan rate of 0.5 mV s<sup>–1</sup> starting from OCP at around –1.1 V in the anodic direction. Before CV, the electrodes were cathodically polarized at –1.3 V for 5 min in order to remove the oxide layer present on the surface of the iron electrode. Galvanostatic discharge was performed at a current density of 50 µA cm<sup>–2</sup> to the potential of –1.3 V vs Hg/Hg<sup>+</sup> starting from –0.42 V on a previously oxidized surface.

After electrochemical testing and before chemical and morphological characterizations by XPS, ToF-SIMS and SEM, the samples were rinsed with ultrapure Millipore® H<sub>2</sub>O and dried with air flow. The samples analysed by XPS, ToF-SIMS and SEM were submitted to 3 complete CVs stopped at OCP in the anodic scan.

A VG ESCALAB 250 spectrometer operating at a base pressure of 10<sup>–9</sup> mbar was used for XPS analysis. An Al Kα monochromatized radiation (*hν* = 1486.6 eV) was employed as X-ray source. Survey spectra were recorded with a pass energy of 100 eV at a step size of 1 eV and high resolution spectra of the C1s, O1s, and Fe2p core level regions were recorded with a pass energy of 20 eV at a step size of 0.1 eV. Peak fitting was performed with the Avantage software (v. 3.13) provided by Thermo Electron Corporation, using a Shirley type background and Lorentzian/Gaussian (70%/30%) peak shapes. The binding energies were calibrated by setting the C1s hydrocarbon (–CH<sub>2</sub>–CH<sub>2</sub>–) peak at 285.0 eV.

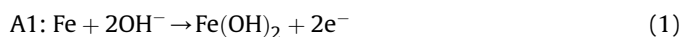
A ToF-SIMS 5 spectrometer (IonToF - Munster, Germany) operating at 10<sup>–9</sup> mbar was used for chemical depth profile analysis. A pulsed 25 keV Bi<sup>+</sup> primary ion source was employed for analysis, delivering 1.2 pA current over a 100 × 100 µm<sup>2</sup> area. Depth profiling

was carried out using a 1 keV Cs<sup>+</sup> sputter beam giving a 70 nA target current over a 300 µm × 300 µm<sup>2</sup> area. The Ion-Spec software from ION-TOF GmbH was used for acquiring and processing the data. Negative ion depth profiles were recorded for better sensitivity to fragments originating from oxide matrices.

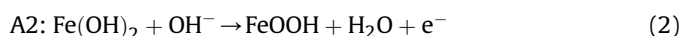
SEM imaging of the iron electrodes before and after electrochemical treatment was performed with a ZEISS Ultra-55 Field Emission Scanning Electron Microscope (FE-SEM, Germany).

## 3. Results and discussion

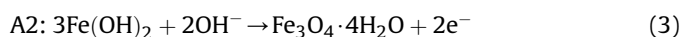
The first three consecutive cyclic voltammograms (CVs) of the iron electrodes in the alkaline electrolyte without and with 0.01 M Na<sub>2</sub>S additives are presented in Fig. 1a and b, respectively, and the first galvanostatic discharge curves are shown in Fig. 1c. In the absence of the Na<sub>2</sub>S additive (Fig. 1a), the magnified CV curves, presented in the inset, show two relatively small and broad anodic peaks A<sub>1</sub> at ~ –0.95 V and A<sub>2</sub> at –0.78 V and two cathodic peaks C<sub>1</sub> at ~ –1.0 V and C<sub>2</sub> at ~ –1.06 V. The C<sub>1</sub> peak becomes better defined at the third CV. These peaks can be attributed to electrochemical oxidation and reduction of the iron electrode. Starting from –1.20 V, an intense and steep cathodic current increase C<sub>3</sub> is observed upon reduction, indicating hydrogen evolution in the alkaline aqueous solution. According to the previous electrochemical studies of iron in alkaline electrolytes [17,25–29], the two anodic peaks correspond to the electrochemical oxidation of iron described by Eqs. (1)–(3) hereafter. The first (A<sub>1</sub>) anodic peak can be attributed to the formation of Fe(II) hydroxide according to [17,30]:



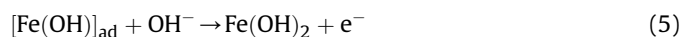
The second (A<sub>2</sub>) anodic peak corresponds to the formation of Fe(III) oxyhydroxide and/or Fe(II, III) oxide according to [25]:



and/or [17,31].

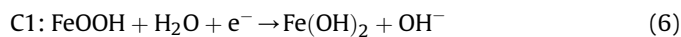


According to some authors [17,27–29], the reaction (1) involves the following partial steps of adsorption of OH<sup>–</sup> ions:



The increase of the A<sub>2</sub>/A<sub>1</sub> intensity ratio suggests that the transformation of Fe(II) to Fe(III) becomes more effective with CV cycling.

In the following cathodic process, the three cathodic peaks correspond to the reduction reaction of the oxidized iron electrode (C<sub>1</sub>, C<sub>2</sub>) and hydrogen evolution in alkaline solution (C<sub>3</sub>). The corresponding reactions can be described by Eqs. (6)–(9).



and/or



The increasing intensity ratio (C<sub>1</sub>+C<sub>2</sub>)/(A<sub>1</sub>+A<sub>2</sub>) suggests that not

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