



Short communication

Feasibility study of hydrogen/iron redox flow cell for grid-storage applications

M. Alon^a, A. Blum^b, E. Peled^{a,*}^a School of Chemistry, Tel Aviv University, POB 39040, Tel Aviv 69978, Israel^b EnStorage Inc., POB 199, Moshav Hazav, Israel

H I G H L I G H T S

- Hydrogen/iron regenerative fuel cell was tested for the first time and showed stable cycle life.
- Electrolytes prepared using different iron salts exhibited different behavior.
- Peak power density was registered at 0.27 W cm⁻².
- Energy conversion of up to 82% was achieved.

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In this study, the hydrogen/iron redox flow cell was evaluated in order to estimate its potential as an energy-storage system. The system was studied for the first time, for energy-storage applications, with electrolytes composed of several different iron salts and their conjugate acids. Cell performance varied with electrolyte composition. Best results were obtained with a solution of iron sulfate in sulfuric acid: stable performance, good capacity utilization, energy-conversion efficiency of up to 82% and a power density of up to 0.27 W cm⁻², with no optimization of cell components. The results show the potential of the hydrogen/iron system as a candidate for energy-storage and further optimization should greatly enhance performance.

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1. Introduction

The depletion of existing energy sources and the rapid increase in the consumption of electricity have led, in recent years, to extensive research on large-scale energy-storage systems. The main uses of these systems include the integration of renewable energy from solar and wind sources and peak leveling by storing power generated during periods of low consumption, and releasing it during peak demand, thus increasing power-generation efficiency and minimizing the need for expensive back-up power generators. New technologies have the potential of becoming a dominant component in energy distribution, such as redox flow batteries (RFB) and regenerative fuel cells (RFC), superconducting magnetic energy storage (SMES) and double-layer capacitors (EDLC) [1].

RFBs and RFCs enable the storing and release of electrical energy by means of chemical species undergoing electrochemical reactions. These chemical species are stored outside the electrochemical cell, enabling the differentiation between stored energy and the rated power, leading to flexible operation compatible with a large number of applications. A typical flow cell consists of two non-consumed electrodes, made of high-surface-area carbon and a separating membrane with selective ion conductivity [2,3]. Extensive research of redox cells is being carried out in an attempt to achieve a reliable and stable system, with long cyclability at an acceptable cost. A few of the most researched redox systems include the vanadium redox battery (VRB), and the iron/chromium and zinc/bromine flow batteries. The iron/chromium system was first developed in 1974 by the American National Aeronautics and Space Administration (NASA) [4,5]. In this system, the cathode electrolyte is composed of Fe(III) ions which undergo reduction while the Cr(II) ions at the anode are oxidized, with most systems using hydrochloric acid as the supporting electrolyte [3]. One challenge of this system is minimizing hydrogen evolution at the

* Corresponding author. Tel.: +972 3 640 8438.

E-mail addresses: alonmeit@tau.ac.il (M. Alon), arnon.blum@enstorageinc.com (A. Blum), peled@tau.ac.il (E. Peled).

chromium electrode during charge, which leads to a decrease in coulombic efficiency and presents the need for a rebalance cell. The vanadium flow battery is one of the most-studied redox systems [6–9]. Since this system uses the same electrolyte on both sides of the cell, it does not suffer from electrolyte degradation following ion transfer. This system is considered to be highly efficient, though presents high sensitivity of system cost to purity of vanadium [10]. Zinc/bromine is another extensively studied system [11–14]. It is considered a hybrid flow battery in which metallic zinc is deposited directly on the anode during the charging process. The zinc is reoxidized during discharge, while bromine is reduced to bromide at the cathode.

In the hydrogen/iron redox flow cell (which is also a regenerative fuel cell) the overall reaction taking place is $\frac{1}{2}\text{H}_2 + \text{Fe}^{+3} \leftrightarrow \text{H}^+ + \text{Fe}^{+2}$, $E^0 = 0.770 \text{ V}$. Advantages of the system include no capacity loss by mixing of cathodic and anodic materials (through the process of reactant recovery) and the use of inexpensive and widely available active materials. The use of hydrogen gas with the Fe(III)/Fe(II) redox couple was examined in a fuel-cell system (discharge only) by Fatih et al. [15], in a single cell with low platinum loading for hydrogen oxidation, carbon felt for iron reduction and a Nafion membrane. In their work, a solution of ferric ammonium sulfate, ferrous sulfate and sulfuric acid was used, with 0.9 M total iron concentration at an Fe(III)/Fe(II) ratio of 9 and at pH 1. The best results show a maximal energy density of 0.17 W cm^{-2} , at 70°C .

The charge-transfer process in the Fe(III)/Fe(II) redox couple is an inner-sphere process [16]; therefore, the charge-transfer kinetics is highly dependent on the nature of the solute iron complex and its electrochemical and physical characteristics. In the presence of different ligands, Fe(III) and Fe(II) ions can take the form of free ions or different complexes in the solution, thus presenting a considerable challenge in the choice of the optimal electrolyte composition and the optimal operating conditions for each composition. In this work, electrolytes containing different iron salts and their conjugate acids were used to evaluate cell performance. Results revealed high efficiencies, good power density, high capacity utilization and good stability and cyclability.

2. Experimental

All electrochemical evaluations were made on a single cell with an active area of 7 cm^2 , as described elsewhere [17]. The cell is composed of graphite flow fields, in interdigit form (flow-through) on the iron side and serpentine (flow-by) on the hydrogen side, with copper current-collector end plates. The hydrogen electrode was fabricated by applying a gas-diffusion layer (GDL) consisting of a mixture of 25% (w/w) PVdF (Kynar) and Vulcan XC-72R on top of a carbon cloth (Ballard) by the doctor-blade method. The catalyst ink consisting of a catalyst powder (PtIr alloy on Vulcan XC-72), 25% (w/w) Nafion (5% in alcohol/water, Aldrich) and isopropanol, was coated with the use of doctor-blade on the previously deposited GDL. Both layers underwent curing and acid treatment ($0.5 \text{ M H}_2\text{SO}_4$, 80°C , 1 h). The process resulted in sublayer loading of about 4 mg cm^{-2} carbon and catalytic loading of $1 \text{ mg PtIr cm}^{-2}$. The iron electrode was fabricated by applying a microporous catalytic layer consisting of a mixture of 10% PVdF (Kynar), MCMB (Osakagas) and catalyst powder (PtIr alloy on Vulcan XC-72) on carbon paper (20% PTFE, Toray) by the doctor-blade method. The layers underwent curing and acid treatment. The process resulted in electrode loading of 2 mg cm^{-2} carbon and metal loading of $0.06 \text{ mg PtIr cm}^{-2}$. A $160 \mu\text{m}$ nano-porous proton-conducting membrane (NP-PCM) [18] was used. The membrane electrode assembly (MEA) was hot-pressed at 100°C . Four electrolyte solutions were prepared with DI water by the use of: $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$

Table 1

Electrolyte compositions, in fully charged and fully discharged states.

Electrolyte code	Comp. fully charged [M]	Comp. fully discharged [M]
1.5 M FeCl_3	1.5 FeCl_3 ; 2 HCl	1.5 FeCl_2 ; 3.5 HCl
1.4 M FeBr_3	1.4 FeBr_3 ; 2 HBr	1.4 FeBr_2 ; 3.4 HBr
1 M FeSO_4	0.5 $\text{Fe}_2(\text{SO}_4)_3$; 2 H_2SO_4	1 FeSO_4 ; 2.5 H_2SO_4
1.5 M FeSO_4	0.75 $\text{Fe}_2(\text{SO}_4)_3$; 2 H_2SO_4	1.5 FeSO_4 ; 2.75 H_2SO_4

(analytical, Sigma) and H_2SO_4 (96%, Sigma), FeCl_3 (analytical, Merck) and HCl (32%, Bio Lab) and lastly Fe_2O_3 (analytical, Sigma) and HBr (48%, Sigma). Electrolyte compositions are shown in Table 1, with the different solutions represented by the iron salt they contain. Hydrogen was generated with the use of an electrolyzer, and hydrogen pressure build-up was controlled by the adjustment of a needle valve placed at the gas exit from the cell. The overpotential developed on the iron electrode was measured with the use of a small piece of carbon paper, coated with a porous GDL layer consisting of 4 mg cm^{-2} XC-72 carbon (0.25 cm^2), submerged in the electrolyte solution tank, near the outlet stream, and connected to a Pt wire (Fe(III)/Fe(II) reference electrode). The voltage was measured between the iron half-cell and the iron reference electrode, expressing the activation, concentration and the ohmic overpotentials developed at the iron electrode. The cells were examined with a Maccor battery-test system, in a polarization procedure to evaluate peak power density and limiting currents. Measurements were made at current densities of up to 0.64 A cm^{-2} which was the maximal current density of the battery-test analyzer channel. Voltage measurements were taken after 30 s at any given current density step, in order to ensure voltage stabilization. Performance was evaluated in a cycle-life procedure of charge and discharge cycles at constant current density, in order to estimate the efficiency, capacity utilization and stability. Hydrogen flow was set at $15\text{--}20 \text{ ml min}^{-1}$ at 1 atm gauge pressure. A $20\text{--}22 \text{ ml}$ of electrolyte solution was circulated through the cell at a flow rate of 18 ml min^{-1} .

3. Results and discussion

3.1. Polarization measurements

Cell polarization was measured for all systems at 40°C . Electrolyte solutions were charged to 0.85–0.9 V before polarization (Fig. 1). Most systems showed good power densities, the highest,

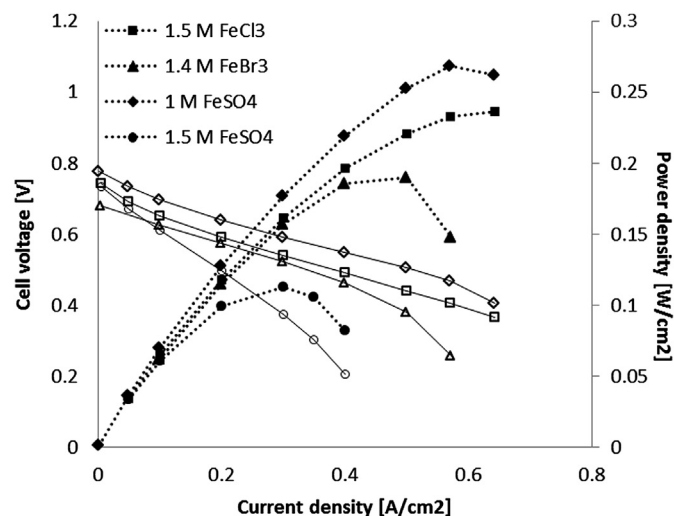


Fig. 1. Polarization curves for different iron electrolytes, taken at 40°C . Full marks represent power density, hollow marks represent voltage.

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