



In-tank hydrogen-ferric ion recombination



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HIGHLIGHTS

- A novel recombination reactor design is proposed.
- High recombination rates were obtained in semi-passive conditions.
- The reactor is predicted to be cost-effective and can fit in a positive tank.

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ABSTRACT

An $\text{H}_2\text{-Fe}^{3+}$ recombination method is being developed for all-iron flow batteries. Working principles are described and a proof-of-concept in-tank reactor is demonstrated. A membrane-less galvanic reactor is characterized using potential, polarization and impedance measurements at hydrogen partial pressures ranging from 0.3 to 11.3 psig. Through a vertical reactor geometry, hydrogen recombination rates of up to 60 mA cm^{-2} were measured at $P_{\text{H}_2} = 4.5 \text{ psig}$ for a reactor with a platinum loading of 3.2 mg cm^{-2} , based on the geometric catalyzed area. This is equivalent to over 375 mA cm^{-2} with respect to the cross sectional area of the reactor at the waterline. This rate is sufficient that the reactor will readily fit inside the positive reservoir of a flow battery. The reactor was found to be resistant to degradation by flooding or catalyst loss.

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1. Introduction

Iron is globally abundant, and its electrodeposition can be carried out efficiently over a wide temperature range, at moderate pH, and with low occurrence of dendritic growth. Hence, all-iron flow batteries can use electrolytes that are safe, sustainable, and low-cost. However, there have been relatively few publications on their development ([1–5]). Here, we consider one of the engineering challenges in such systems, which is to maintain the balance of active species in the electrolyte. We describe a sealed iron flow battery that incorporates $\text{H}_2\text{-Fe}^{3+}$ recombination to provide the necessary balance.

The electrode reactions during charging and discharging of all-iron flow batteries are given in Table 1. However, iron deposition at the negative electrode (during battery charging) is always accompanied by some hydrogen evolution. One of the challenges in developing all-iron flow batteries has been the electrolyte imbalance that results from this undesired side reaction [6]. Over time,

the hydrogen side reaction causes the electrolyte to become imbalanced in two ways; firstly, the loss of protons from solution causes the negative electrolyte pH to rise, promoting the formation of solid hydroxide precipitates usually abbreviated as $\text{Fe}(\text{OH})_3$ ([7–9]). Formation of such materials reduces capacity and leads to a sludge that can hinder electrolyte flow, lower the electrode area and damage the porous separator. Secondly, the positive electrolyte becomes over-concentrated in ferric ions (Fe^{3+}), rendering the battery unable to charge when no ferrous ions are available to be oxidized at the positive battery electrodes. The latter problem (over-concentration of Fe^{3+}) was addressed in the NASA iron-chromium system by using an $\text{H}_2\text{-Fe}^{3+}$ rebalancing fuel cell [10]. However, the fuel cell recombination system was eventually abandoned due to problems associated with flooding and platinum dissolution in the highly acidic electrolytes used [11].

Recently, it was shown that certain complexing ligands such as glycine can be used to help reduce hydrogen evolution during iron electrodeposition [2]. However, it was not possible to completely eliminate hydrogen evolution, so there will always be some hydrogen generation during battery charging. For long-term electrolyte balancing, therefore, it is necessary to bring all the excess hydrogen and ferric ions back into chemical balance via Equation

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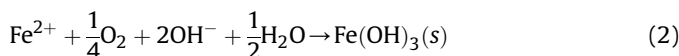
Table 1
All-iron battery reactions.

Electrode	Reaction	E^0 (V)
Negative	$\text{Fe}^{2+} + 2e \rightleftharpoons \text{Fe}^0$	-0.44
Positive	$\text{Fe}^{3+} + e \rightleftharpoons \text{Fe}^{2+}$	0.77
Overall	$3\text{Fe}^{2+} \rightleftharpoons \text{Fe}^0 + 2\text{Fe}^{3+}$	1.21

(1), the $\text{H}_2\text{-Fe}^{3+}$ recombination reaction.



While other researchers have described the use of PEM fuel cells ([10,12]), electrolyzers ([11,13]) trickle bed reactors [14], and other flow-through cells [15] to carry out similar processes, such approaches often require additional pumps, externally-supplied reactants or complex control systems. In addition, many of these methods vent hydrogen to the atmosphere. Since iron battery electrolytes are inherently buffered, accurate and continuous pH measurement is difficult and so control systems based on pH probes are challenging for electrolyte control. For practical applications, it is desirable to minimize the complexity and cost associated with the recombination system. Furthermore, the flow battery system should be sealed to prevent hydrogen losses as well as the oxidation of ferrous ions (Fe^{2+}) by air. In iron electrolytes, for example, the presence of oxygen can lead to the formation of solid ferric hydroxide species according to Equation (2) [16].



An in-tank recombination reactor can have important advantages including simplicity, low-cost, and it avoids adding volume to the system. Recently, Whitehead and Harrer investigated an in-tank $\text{H}_2 - \text{VO}_2^+$ recombination reactor for vanadium flow batteries utilizing a horizontal floating reactor based on catalyzed carbon paper [17]. A horizontal reactor geometry, however, is limited to the cross-sectional area of the electrolyte tank, which may not be adequate for all applications. Furthermore, thin horizontal reactors may be more prone to flooding, and the carbon paper reactor also required membrane filtration to mitigate problems with catalyst adhesion. In order to help address some of these issues, this study describes an improved $\text{H}_2\text{-Fe}^{3+}$ recombination reactor designed for sealed iron flow battery systems but with broader possible applications as well. We present a reactor design wherein the reactions take place on a vertically-oriented galvanic cell (or capillary-action galvanic reactor, CGR) that uses carbon felt as illustrated in Fig. 1. In this configuration, we consider the performance relative to A_{geo} , which is the catalyzed area for hydrogen oxidation, and relative to A_{cs} , which is the cross sectional area of the felt at the waterline. Since the area at the waterline is limited by the size of the electrolyte reservoir, sufficiently high recombination rates relative to the waterline area are required for an in-tank reactor.

The reactor oxidizes hydrogen in the gas phase while simultaneously reducing ferric ions in solution. The vertical orientation allows for greater reaction rates (especially in terms of the cross sectional area, A_{cs}) than could be obtained using a horizontal geometry. In a horizontal reactor, $A_{\text{geo}} = A_{\text{cs}}$, but with a vertical reactor it possible to have $A_{\text{geo}} > A_{\text{cs}}$, analogous to using fins to increase area in heat transfer applications. Furthermore, the CGR design operates at low hydrogen partial pressures (0–50 mol% H_2), and without the need for any membrane materials. We report here the characterization of the CGR using several methods, and demonstrate pressure control in a sealed all-iron flow battery. The CGR should also be

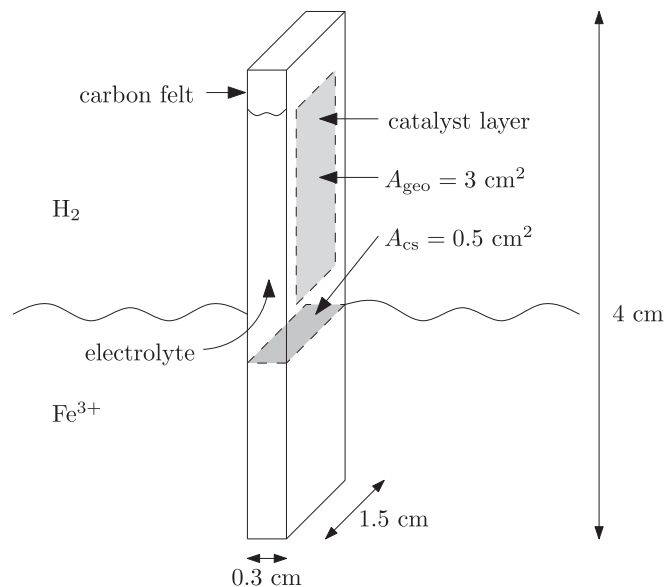


Fig. 1. Schematic of a capillary-action galvanic reactor (CGR) design to oxidize gaseous hydrogen and reduce dissolved metal ions. A_{geo} is the catalyzed area for hydrogen oxidation. A_{cs} is the cross sectional area of the felt at the waterline. Floats (not shown) ensure that the catalyzed area remains above the liquid level.

applicable to other aqueous flow batteries that produce hydrogen as a by-product during battery charging.

2. Materials & methods

A vertically-oriented reactor was developed and characterized in sealed, pressurizable vessels ($V = 212$ mL). The ionic pathway was established through capillary wetting within the pores of the carbon felt. Hydrogen is oxidized on the upper half of the CGR at the available triple-point sites. Protons and electrons, liberated by hydrogen oxidation, are transported downward (in the “in-plane” direction) into the positive electrolyte, where aqueous ferric ions (Fe^{3+}) are reduced to ferrous ions (Fe^{2+}). The reactor was fabricated using a carbon felt substrate (Cera Materials PAN-based graphitic felt, thickness = 1/8 in) that was pre-treated by heating in air at 400 °C for 24 h. The upper half of the CGR was coated with a layer of Pt/C (E-Tek, Inc., 40 wt% Pt on Vulcan XC-72), which had been painted onto the felt as an ink using PVDF as a binder. The ink solvent was n-methyl-2-pyrrolidone (NMP), and the catalyst loading was 3.2 $\text{mg}_{\text{Pt}} \text{cm}^{-2}$ based on the geometric area of 3 cm^2 . The cross-sectional or horizontal area was 0.5 cm^2 , so in this case $A_{\text{geo}}/A_{\text{cs}} \approx 6$.

The $\text{H}_2\text{-Fe}^{3+}$ recombination reaction on the CGR was then investigated in several different ways. The first approach used a three-electrode apparatus (see Fig. 2), which was used to measure the hydrogen polarization and impedance spectra in a NaCl solution as a symmetric hydrogen cell. As hydrogen was oxidized in the gas-phase portion of the CGR, the platinum mesh counter electrode carried out proton reduction; hence, the total hydrogen content was maintained constant. In Fig. 2, the counter electrode was a platinum mesh and the reference electrode was Ag/AgCl (3.0 M NaCl). Cyclic voltammetry was used to investigate the hydrogen oxidation behavior at different partial pressures of hydrogen from 0.3 to 11.3 psig. The performance of the CGR was then investigated in several different ways. First, a three-electrode apparatus (see Fig. 2) was used to measure the hydrogen polarization and impedance spectra in a NaCl solution. As hydrogen was oxidized in the gas-phase portion of the CGR, the platinum mesh

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