In-tank hydrogen-ferric ion recombination

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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 0.3-11.3 psig. Through a vertical reactor geometry, hydrogen recombination rates of up to 60 mAcm^{-2} were measured at $P_{\text{H}_2}=4.5$ psig for a reactor with a platinum loading of 3.2 mgcm^{-2} , based on the geometric catalyzed area. This is equivalent to over 375 mAcm^{-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.

Keywords: all-iron flow battery, recombination, rebalancing

1. Introduction

Iron is globally abundant, and its electrodeposition can be carried out efficiently over a wide temperature range, at moderate $p\text{H}$, 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.

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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

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 $p\text{H}$ 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 H_2 - 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 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 $p\text{H}$ measurement is difficult and so control systems based on $p\text{H}$ 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 Figure 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 section area, A_{cs}) than could be obtained using a horizontal geometry. In a horizontal reactor, $A_{geo} = A_{cs}$, but with a vertical reactor it possible to have $A_{geo} > A_{cs}$, 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 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 hours. 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 $3.2 \text{ mg}_{Pt} \text{ cm}^{-2}$ based on the geometric area of 3 cm^2 . The cross-sectional or horizontal area was 0.5 cm^2 , so in this case $A_{geo}/A_{cs} \approx 6$.

The H_2 - Fe^{3+} recombination reaction on the CGR was then investigated in several different ways. The first approach used a three-electrode apparatus (see Figure 2), which was used to measure the hydrogen polarization and impedance spectra in an NaCl solution as a symmetric hydrogen cell. As hydrogen was oxidized in the gas-phase portion

Figure 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.

of the CGR, the platinum mesh counter electrode carried out proton reduction; hence, the total hydrogen content was maintained constant. In Figure 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 Figure 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 counter electrode carried out proton reduction; hence, the total hydrogen content was constant. The potential of the CGR was measured with respect to a Ag/AgCl reference electrode. Cyclic voltammetry and AC impedance were used to investigate the hydrogen oxidation behavior at different partial pressures of hydrogen from 0.3 to 11.3 psig.

The second approach used a one-electrode configuration with a solution containing 1 M FeCl_3 , 1 M FeCl_2 , and 2 M NaCl (see Figure 3). The reaction rate in this configuration was measured by monitoring the gas pressure. The CGR was partially submerged in

Figure 2: Schematic of the three-electrode apparatus used to characterize the upper half (the hydrogen electrode) of the CGR in 2 M NaCl ($pH = 1.4$) at several different partial pressures of hydrogen. The reference electrode was Ag/AgCl (3 M NaCl), and the counter electrode was a platinum mesh.

Figure 3: Schematic of the one-electrode apparatus used to obtain the H_2 - Fe^{3+} recombination rate.

the electrolyte such that the lower half was in solution to carry out Fe^{3+} reduction and the upper half was in the reactor headspace to facilitate hydrogen oxidation. The headspace was purged with nitrogen, then hydrogen was pulse-injected into the reservoir at a partial pressure of $P_{H_2} = 4.5$ psig. Following the hydrogen injection, the pressure was recorded over time until all of the hydrogen had been consumed (Omega PX-302 digital transducer).

Figure 4: Use of the CGR in a complete flow battery system. A headspace connection tube (OD = 0.25 in, length $\approx 12''$) provided a pathway for hydrogen to diffuse from the negative to the positive reservoir.

After injecting hydrogen, the pressure began to drop due to the hydrogen being consumed by oxidation on the CGR catalyst layer. Simultaneously, ferric ions were reduced at the felt surface that extended down into the electrolyte. The recombination reaction rate, i_{H_2} (Acm^{-2}) was calculated from the slope of the pressure drop using Equations 3 and 4, where $n=2$ is the number of electrons involved in the reaction, F is the Faraday constant ($96,485 \text{ Cmol}^{-1}$), V_{hs} is the headspace volume (L), R is the universal gas constant ($0.08206 \text{ Latmmol}^{-1}K^{-1}$), and T is the temperature (293 K).

$$i_{geo} = -\frac{nFV_{hs}(dP/dt)}{A_{geo}RT} \quad (3)$$

$$i_{cs} = -\frac{nFV_{hs}(dP/dt)}{A_{cs}RT} \quad (4)$$

A sealed all-iron flow battery system (see Figure 4) was cycled both with and without a CGR for comparison of the pressure profiles. In each cycling test, the battery was charged and discharged at $\pm 20 \text{ mAcmm}^{-2}$, where each charge duration and each discharge duration was one hour. The battery electrodes consisted of flat graphite plates with an area of 6.25 cm^2 . A porous separator was used (Daramic SLI 175). The system operated at ambient temperature, and both electrolytes were pumped at 50 mL/min using a peristaltic pump. Both electrolytes contained 1 M FeCl_2 and 2 M NaCl , and

the positive electrolyte also contained 0.5 M FeCl_3 . Each reservoir contained 100 mL of electrolyte, and the headspace volumes were connected using 1/4" tubing in order to create a pathway for hydrogen diffusion from the negative to the positive reservoir.

3. Results & Discussion

The three-electrode apparatus was used to measure open-circuit potentials as well as carrying out voltammetry and EIS experiments in sodium chloride solutions adjusted to $\text{pH}=1.4$ with HCl . The Nernstian behavior of the open-circuit potential measurements confirmed that the upper half of the CGR operated as expected with respect to the hydrogen partial pressure.

Longer duration experiments showed that the reactor was resistant to degradation by flooding or loss of catalyst. In several experiments, the performance appeared to increase over time, perhaps due to improved wetting of the felt fibers. This effect applied both when carrying out the recombination reaction as well as during hydrogen oxidation in the three electrode apparatus in the absence of iron in solution.

Results from voltammetry and EIS experiments are shown in Figures 5 and 6. In all runs, the gas composition contained 1 atm of nitrogen plus some additional hydrogen ranging from 0.3-8.0 psig. It was observed that hydrogen partial pressure had a significant effect on the hydrogen electrode polarization up to about $P_{\text{H}_2}=8$ psig, beyond which the rate became limited by other factors such as ohmic losses or ferric ion concentration polarization. An apparent limiting hydrogen current was observed at the lowest partial pressure of $P_{\text{H}_2}=0.3$ psig consistent with a low frequency mass transfer loop observed in the EIS response.

Transient measurements of the hydrogen partial pressure, as measured using the apparatus shown in Figure 3, were used to determine the rate of the recombination reaction with a sealed system. It was assumed that any measured pressure drop (after hydrogen addition) was due to hydrogen consumption via Equation 1, i.e., that there were no significant leaks, and this assumption was validated before each test by nitrogen pressure testing. When only nitrogen was present, the pressure did not change over time.

When only nitrogen was present in the vessel, the pressure remained constant, indicating there were no significant leaks. After introducing hydrogen, the pressure immediately

Figure 5: Impedance behavior as a function of hydrogen partial pressure (P_{H_2}) as measured using the apparatus shown in Figure 2. The low frequency response indicated a mass-transfer resistance loop that decreased with increasing P_{H_2} from 0.2 up to 8.2 psig.

Figure 6: Voltammetric response in unstirred solution as a function of hydrogen partial pressure (P_{H_2}) as measured using the apparatus shown in Figure 2.

began to drop until all the hydrogen had been consumed. Recombination rates of up to 180 mA was observed at $P_{H_2} = 4.5$ psig, which was clearly much greater than the limiting current of ferric ion diffusion based on the cross-sectional area ($A_{cs}=0.5 \text{ cm}^2$). That is, assuming a horizontal reactor with $A=0.5 \text{ cm}^2$ and a limiting Fe^{3+} current density of 30 mAcm^{-2} (a reasonable value for a one electron reaction occurring at a smooth elec-

Figure 7: Hydrogen oxidation current densities relative to the catalyzed and cross sectional areas as shown in Figure 1 and calculated using Equations 3 and 4.

trode with significant electrolyte flow over the electrode surface), the maximum possible current would have only been 14 mA. Using Equations 3 and 4, the observed current of 180 mA corresponds to approximately 60 mAcm^{-2} based on the geometric catalyzed area and 375 mAcm^{-2} based on the cross-sectional (horizontal) area (see Figure 7). This current density is over an order of magnitude greater than that reported for the reactor described in Ref. [17], despite operation at a lower concentration of hydrogen (less than 24 mol% H_2 in this study). This result indicates that the reactions are distributed over the wider area available as a result of the vertical orientation of the reactor.

When implemented in an iron flow battery system, the reactor was able to effectively control the pressure, as shown in Figure 8. When the reactor was not used, the pressure increased with each cycle. When the reactor was installed in the positive reservoir, however, the pressure initially rose at the same rate but then began to decrease and level off as hydrogen diffused through the headspace connection and the recombination reaction took effect. Without the CGR installed, there was still some decline in the slope over time, and this can be attributed mainly to increasing electrolyte pH. The difference between the slopes with- and without the CGR can then be attributed to hydrogen consumption.

Considering the reaction rates demonstrated here for the CGR, it is now feasible

Figure 8: Comparison of pressure profiles during continuous battery cycling at $\pm 20 \text{ mAcm}^{-2}$ using the apparatus illustrated in Figure 4. The charge and discharge durations were each one hour.

to implement in-tank recombination for systems like the all-iron battery that have 1-5% coulombic losses to hydrogen generation on charge. A CGR system operating as described here would require $\approx 40\%$ of the available electrolyte surface area. In addition, with a reasonable reduction in the platinum loading to 0.2 mgcm^{-2} , we estimate that the materials cost for catalyst and felt would be $< \$10$ per kW of battery power in an all-iron system.

4. Conclusions

An $\text{H}_2\text{-Fe}^{3+}$ recombination reactor was developed for a sealed all-iron flow battery system. Although hydrogen suppression additives or acid additions can be used to minimize the effects of hydrogen evolution for finite periods of time, these approaches are insufficient to ensure long-term electrolyte balance. To control $p\text{H}$ and ferric ion concentration, therefore, a hydrogen recombination strategy must be implemented. Since hydrogen and ferric ions become out of balance in proportion to one another, a chemical balance can be achieved in a sealed recombinant flow battery system as described in this work without the need for an external control system. This study describes a simple, in-tank galvanic reactor that can carry out the recombination reaction without the need for additional pumps, control systems or membranes. A recombination current of up to 60 mAcm^{-2} (based on the platinum catalyzed area) or 375 mAcm^{-2} (based on

the horizontal area taken up by the reactor at the waterline) was observed with light stirring in 1.0 M FeCl₃ at P_{H_2} =4.5 psig. The reactor was shown to be stable and resistant to flooding, and there was no evidence of any issues associated with loss of catalyst layer adhesion. Future studies will look in more detail at the wicking behavior, current distribution, non-Pt based electrocatalysts, and scale-up. With continued research and development, the CGR holds promise as an effective tool for rebalancing electrolytes and hence extending lifetimes in sealed flow batteries. The methods described here can also apply to vanadium, iron-chromium, zinc-bromine, and other battery chemistries.

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Figure Captions

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