Slurry electrodes for iron plating in an all-iron flow battery

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HIGHLIGHTS

- Slurries are investigated as negative electrodes in all-iron flow batteries.
- Current distribution is modeled as a function of area and electrical conductivity.
- MWCNTs slurries contained >95% of battery charge (as opposed to current collector).
- Slurry electrodes can be effectively used to decouple all-iron flow batteries.

ARTICLE INFO

ABSTRACT

Slurry electrodes are investigated in order to decouple the energy storage capacity from the power delivery capability in an all-iron flow battery. For the slurry electrode to perform effectively, the battery negative reaction must occur on the slurry particles at reasonably high current densities. Mathematical modeling is used to investigate the current distribution in a slurry electrode as a function of the slurry specific area and electrical conductivity in order to achieve >95% plating in the slurry electrode (not on the flat plate) at > 200 mA cm^{-2}. From the mathematical modeling, MWCNTs are selected to demonstrate slurry electrode performance. The experimental performance of all-iron batteries charged using the MWCNT slurry electrodes is found to improve while increasing the battery state-of-charge. Two possible mechanisms contributing to this effect are an increase in electronic conductivity of the slurry and an increase in plating kinetics. After cycling the battery, <5% of the total battery charge was observed to have plated onto the current collector.
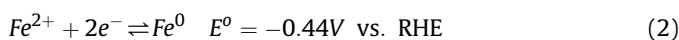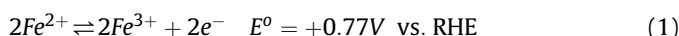
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1. Introduction

Redox flow batteries (RFBs) have seen a surge of interest over recent years for their ability to provide ancillary services to the electric grid which could lead to increased robustness, flexibility, and the ability to rely on intermittent renewable energy sources such as wind and solar [1–5]. Traditional RFBs, including the iron–chromium [6], iron–vanadium [7,8], bromide-polysulfide [9], and all-vanadium [10] systems, store energy chemically in electroactive species contained in electrolytes that are stored in external reservoirs. During operation, the electrolyte is pumped through the RFB where the chemical energy is directly converted to electrical energy. The architecture of RFBs allows the energy storage capacity (dependent on the amount of active species) to be scaled independently of the power rating (dependent on the area of the

RFB conversion device) leading to flexible operation and implementation. Despite the advantages, the cost [11], abundance, and toxicity of the active species have hindered the market penetration of these systems.

An attractive alternative to the traditional RFB chemistries is the all-iron flow battery [12] because iron, the only active element, is low cost, abundant, and environmentally benign. Equations (1) and (2) describe the positive and negative reactions in the all-iron flow battery, respectively. On charge, ferrous ions (Fe^{2+}) are oxidized to ferric ions (Fe^{3+}) in the positive half-cell while ferrous ions are reduced to iron metal in the negative half-cell. The all-iron battery has a standard cell voltage of 1.21 V.

$$2Fe^{2+} \rightleftharpoons 2Fe^{3+} + 2e^- \quad E^o = +0.77V \text{ vs. RHE} \tag{1}$$

$$Fe^{2+} + 2e^- \rightleftharpoons Fe^0 \quad E^o = -0.44V \text{ vs. RHE} \tag{2}$$

RFBs typically employ electrodes made of porous carbon structures (e.g. felts, cloths, or papers) fixed in the electrochemical

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device. When using these stationary electrodes in the all-iron flow battery, iron metal is plated into their structure and subsequently stored in the electrochemical cell. For a majority of grid applications, it is expected that an energy to power ratio of 3–8 h is required [2]. Because iron metal is stored in the electrochemical cell, the conventional all-iron battery is limited to <4 h of energy storage at reasonably high current densities [13]. Existing capital cost models suggest that current densities above 200 mA cm^{-2} will be necessary to achieve acceptable stack costs for large scale adoption of flow batteries [11,14,15]. In order to have a battery with the advantages inherent to traditional flow battery architectures and the advantages of the all-iron chemistry, a different electrode structure must be employed that enables higher energy storage to power ratios. One such option is the slurry electrode.

Slurry electrodes are made by suspending solid, electronically conductive particles in the ionically conducting electrolyte and have been studied for a variety of electrochemical applications [17–23]. During charge and discharge, the electrolyte is pumped through the electrochemical cell as in normal RFB operation. However, when using slurry electrodes, the solid particles are carried by the electrolyte into and out of the electrochemical cell. If the volume fraction of the solid particles is high enough, a continuous electrically conductive network forms [24,25]. This allows the redox reaction to occur on the surface of the slurry particles. When slurries are employed as the negative electrode of the all-iron flow battery, iron metal is plated onto the slurry particles. As the slurry is circulated out of the electrochemical cell back into the external reservoir, the iron metal is carried with the particles, enabling the energy storage capacity to be decoupled from the power rating. Additional advantages of slurry electrodes include their ability to have high surface areas, simple manufacturing/assembly, and ease of maintenance/recycling through filtering. Previous studies have investigated the ferrous/ferric redox couple on slurry electrodes [23]. This paper reports results of an investigation of the performance of slurry electrodes in the full all-iron flow battery while focusing on the plating of iron metal into the negative slurry electrode.

2. Analytical current distribution models

Mathematical modeling of the slurry electrode in the negative half-cell was performed in order to permit the selection of viable candidate slurries. The selection of an appropriate particle to use as the flowable slurry electrode was performed with regards to two principal performance metrics.

The first performance metric was related to the achievable current density. Cost models have shown that for the all-iron slurry battery to be practical that the battery needs to be able to support a current density of 200 mA cm^{-2} at a voltaic efficiency of at least 70% [11,14,15]. Given the 1.2 V cell potential of the all-iron battery, this means that the desired current density must be achieved with at most 212 mV of total overpotential across the entire cell.

The second performance metric is related to the amount of plating that occurs onto the current collector. If plating occurs onto the current collector and not onto the slurry particles, then the energy density and power density of the battery are no longer decoupled. As decoupling is a desirable trait for grid-scale energy storage, a criterion was established demanding that less than 5% of the total metal plating should occur onto the current collector.

The slurry characteristics necessary to match the performance metrics were examined using standard one-dimensional macrohomogeneous porous electrode equations [26,27]. The governing equations are identical to those used by Fleischmann and Oldfield for fluidized bed electrodes [28]. The kinetics of the plating reaction were assumed to be linear, resulting in the following equations:

$$\sigma \frac{d^2\Phi_1}{dx^2} - a_0 z f i_o \eta = 0 \tag{3a}$$

$$\kappa \frac{d^2\Phi_2}{dx^2} + a_0 z f i_o \eta = 0 \tag{3b}$$

Here, σ is the electronic conductivity of the slurry phase, κ is the ionic conductivity of the solution phase, Φ_1 is the potential of the slurry phase, Φ_2 is the potential of the solution phase, a_0 is the specific area of the slurry electrode, z is the number of electrons involved in the plating reaction, $f=FR^{-1} T^{-1}$ is related to Faraday's constant, i_0 is the exchange current density, x is the spatial coordinate across the channel gap, $\eta=\Phi_1-\Phi_2-U_{ref}$ is the overpotential, and U_{ref} is the open-circuit potential of the electrode reaction relative to a suitable reference electrode such that the overpotential is zero at equilibrium. Effects such as mass transfer overpotentials or advectively-induced capacitive currents are ignored by this model, but it is believed to capture the dominant behavior associated with slurry electrodes in the presence of fast faradaic reactions.

In order to account for the fact that reactions can occur on both the current collector plate and the slurry particles, the standard boundary conditions used by Fleischmann and Oldfield needed to be altered. The modified boundary conditions at $x = 0$ (the current collector) and $x = \delta$ (the location of the separator) take the form:

$$\frac{d\Phi_1}{dx} = -\frac{(i_d - \xi z f i_o \eta_o)}{\sigma}; \frac{d\Phi_2}{dx} = \frac{-\xi z f i_o \eta_o}{\kappa} \quad \text{at } x = 0 \tag{4a}$$

$$\frac{d\Phi_1}{dx} = 0; \frac{d\Phi_2}{dx} = \frac{-i_d}{\kappa} \quad \text{at } x = \delta \tag{4b}$$

Here, i_d is the applied current density, ξ is the roughness factor of the current collector, and η_0 is the overpotential at $x = 0$. The total overpotential across the half-cell can be described as $\eta_{tot}=\Phi_1(0)-\Phi_2(\delta)-U_{ref}$. An additional factor accounting for the area of the current collector that is occluded by the presence of the slurry could also be included in the boundary conditions, but for low volume fraction slurries (like those in this paper), this effect is believed to be negligible.

The slurry properties that affect the achievement of the above performance metrics are the specific interfacial area and the electronic conductivity. Using typical values for cell dimensions, iron plating reaction kinetics, and electrolyte properties (see Table 1), Equations (3a) and (3b) were solved in order to generate maps of the combinations of σ and a_0 that satisfy the metrics. These maps are shown in Fig. 1. Regions corresponding to the polarization metric (<100 mV of overpotential in the negative half cell at 200 mA cm^{-2} or higher) and to the current collector plating metric are both included. Any viable slurry must lie within the bounds of both regions.

As shown in Fig. 1, slurries made with MWCNTs are predicted to be able to achieve both performance metrics [23]. It is likely that other less expensive particles can also match the criteria, but, as a proof of concept, the MWCNT slurry was adopted to permit the

Table 1
Parameters used for slurry electrode model.

Parameter	Value
δ	0.1 cm
z	2 $\frac{\text{mole e}^-}{\text{mole Fe}^{2+}}$
ξ	10 cm^2 cm^{-2}
i_0	1 mA cm^{-2}
κ	200 mS cm^{-1}
η_{tot}	100 mV