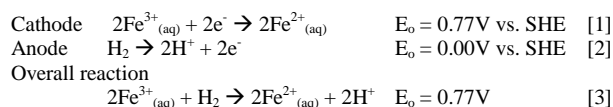Assessment of the Iron-Ion/Hydrogen Redox Flow Cell

Michael C. Tucker*, Kyu Taek Cho, Venkat Srinivasan, Philip N. Ross, and Adam Z. Weber
Lawrence Berkeley National Laboratory
1 Cyclotron Rd, Berkeley CA 94720

There is currently a resurgence of interest in redox flow cells for energy storage, especially at the grid-scale due to the increase of variable renewable-energy generation. Redox flow cells use electrochemically-active anode and cathode species to store energy. Typically, the active species are dissolved in liquids that are pumped from reservoirs through the cell, which contains electrodes and an ion-exchange or microporous membrane. The primary qualifications for adoption of redox flow cells for grid storage are cost, reliability, and safety.

In this work, we report development of the iron-ion/hydrogen redox flow-cell system, depicted in Figure 1. The primary motivation for developing the iron-ion/hydrogen flow-cell system is that the active materials offer low toxicity and cost relative to common flow-battery materials such as chromium, vanadium, bromine, chlorine, and lead. For example, iron chloride is two orders of magnitude less expensive than vanadium pentoxide. A secondary motivation is to leverage the highly developed technology of PEM fuel cells to accelerate development of this similar system.

In this system, the anode active species is hydrogen gas and the cathode active species is the Fe^{2+}/Fe^{3+} couple, present as an aqueous salt. During discharge, the hydrogen is oxidized to protons and the iron is reduced:

Cathode $2Fe^{3+}_{(aq)} + 2e^- \rightarrow 2Fe^{2+}_{(aq)}$ $E_o = 0.77V$ vs. SHE   [1]
Anode $H_2 \rightarrow 2H^+ + 2e^-$ $E_o = 0.00V$ vs. SHE   [2]
Overall reaction
            $2Fe^{3+}_{(aq)} + H_2 \rightarrow 2Fe^{2+}_{(aq)} + 2H^+$ $E_o = 0.77V$ [3]

The iron-ion/hydrogen redox flow cell has been tested with a variety of catholyte solution compositions. It was found that iron-nitrate solutions rapidly lose capacity, possibly via reduction of the nitrate ion. Stable cycling was achieved with iron-chloride and iron-sulfate solutions, as shown in Figure 2. Although the cycling stability and utilization were marginally better for iron-sulfate solutions, the high viscosity and poor charge polarization lead us to conclude that iron chloride is the most promising salt of those studied herein.

The iron-ion/hydrogen redox flow cell was operated with a variety of porous-carbon cathode electrodes, membrane types, and catholyte-solution compositions at ambient conditions. The largest impact on performance came from optimization of the catholyte-solution composition. It is found that the concentration of HCl supporting electrolyte has a dramatic impact on charging performance and OCV, as shown in Figure 3. Charge currents in excess of 1 A/cm^2 are achieved for 4 and 6 M HCl. The maximum discharge power density, 257 mW/cm^2, is achieved for 0.9M iron chloride with 0.9M HCl. Based on these results we believe further optimization of solution chemistry will be a fruitful path for future work.

Acknowledgements
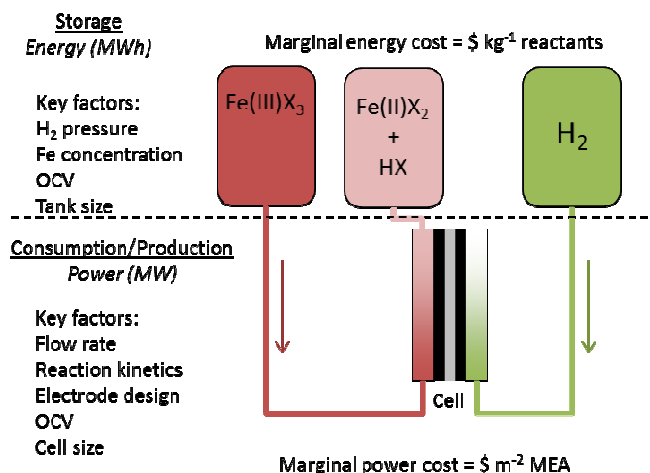
Figure 1. Schematic of iron-ion/hydrogen flow cell

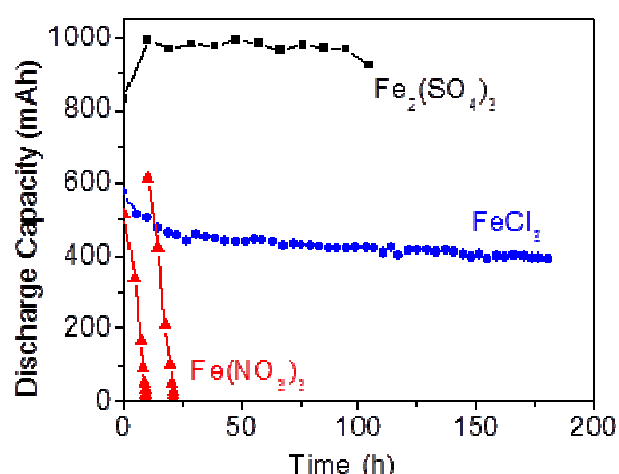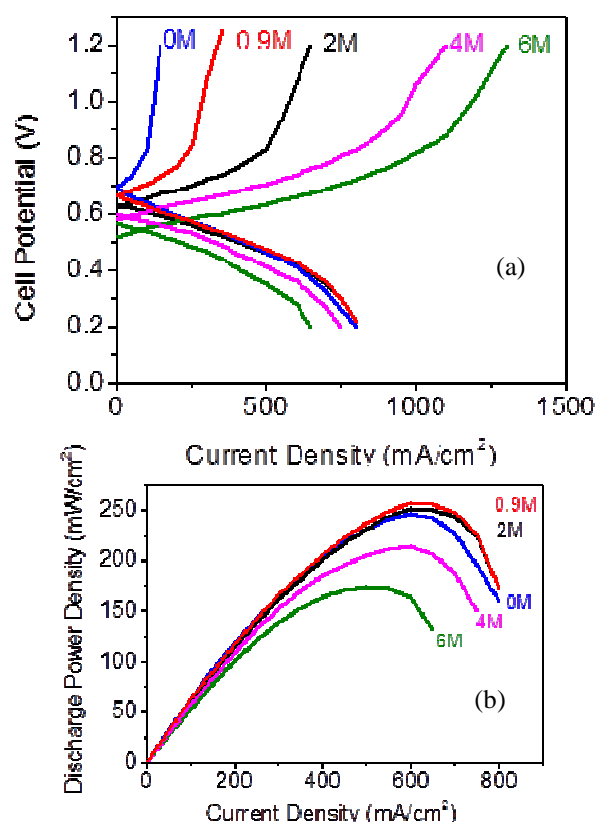Figure 2. Cycling of various iron salt solutions at 25mA/cm^2

Figure 3. (a) Polarization and (b) power density for solutions of 0.9M FeCl$_3$ and various concentrations of HCl.