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All-Iron Redox Flow Battery Tailored for Off-Grid Portable Applications

Michael C. Tucker, Adam Phillips, and Adam Z. Weber

Abstract

An all-iron redox flow battery is proposed and developed for end-users without access to an electricity grid. The concept is a low-cost battery for which the user assembles, discharges, and then disposes of the active materials. The design goals for this application are: (1) minimize upfront cost, (2) maximize discharge energy with respect to the cost of consumable materials, and (3) limit the choice of materials to those that are non-toxic and environmentally benign. This is a different set of goals than are typically considered for electrochemical battery technology, which provides the opportunity for a novel optimization solution. In this paper, various electrolyte compositions and separator and electrode materials are screened for downselection based on cost, toxicity, and performance. The selected materials are: low carbon steel negative electrode, paper separator, porous carbon paper positive electrode, and electrolyte solution containing 0.5 M $\text{Fe}_2(\text{SO}_4)_3$ active material and 1.2 M NaCl supporting electrolyte. With these materials, an average power density around 20 mW cm^{-2} and a maximum energy density of 11.5 Wh L^{-1} are achieved. A simple cost model indicates the consumable materials would cost \$6.45 kWh^{-1} , or only \$0.034 per mobile phone charging session.

1.0 Introduction

Access to energy is critically lacking throughout the developing world.^[1] Purchasing electricity for basic household needs such as LED lighting, mobile phone charging, and radio is expensive and difficult. Solar home systems are beyond the means of most of these households, and charging mobile phones at pay-per-

charge kiosk businesses is time consuming and expensive, costing about \$0.25 per charge. Kerosene lighting is also expensive, with fuel costs around \$4 per month for a household.^[2]

The present work assesses the technical and economic feasibility of an extremely inexpensive, long shelf-life, nontoxic battery concept proposed to enable access to electricity for typical bottom-of-the-pyramid consumers. These consumers are extremely price conscious, have a real unmet need, and do not generally have access to waste-stream recycling. Spent batteries are expected to be disposed of in the normal household waste stream. In many areas, this means spent material will be dumped outside the dwelling or into open-pit sewers, making selection of environmentally benign materials just as important as human health considerations.

To address these opportunities and constraints, we propose a low-cost, chemically-rechargeable battery composed of materials that are benign. The goal is an intuitive and affordable product that allows users to generate a small amount of electricity on-demand, in their own home (e.g. for LED lighting or mobile phone charging). The user will insert active materials into the cell periodically, before every discharge, and spent material is simply disposed. The cell is “recharged” by replacing the active materials, as opposed to electrochemical charging *via* external electricity supply. This frees the designer to optimize discharge performance, with no need to address electrochemical charge performance. Further benefits expected of this design include a long shelf life, as active materials are not in contact with each other until the time of use, and reduced delivery costs, as there is no water or other solvent weight to be transported from the manufacturing facility to the end user.

The product concept includes a durable cell housing that accepts the consumable cell materials, including anode, cathode, and separator, and when closed holds them in compressed contact. The end-user would do as much assembly as is practical to minimize up-front cost. The housing also has electrical contacts for the anode and cathode, and ports for the catholyte to enter and exit. The user is responsible for mixing the

catholyte salt, provided as a packet or tablet, with locally-available water and pouring into the cathode vessel. The exiting solution can be collected and passed through the cell again to increase total utilization of the chemicals. The cell is comprised of inexpensive materials, and many of the materials are replaced at regular intervals, some before every discharge, to relieve the constraint of long-term stability and cycle life.

The design goals for this application are: (1) minimize upfront cost, (2) maximize discharge energy with respect to the cost of consumable materials, and (3) limit the choice of materials to those that are non-toxic and environmentally benign. This is a different set of goals than are typically considered for electrochemical battery technologies, and provides the opportunity for a novel optimization solution.

To meet the above targets, an all-iron system that uses iron metal and ferric ions is attractive. Iron, among the common metals, is notable for its low cost, low health risk, and ubiquitous availability. The all-iron redox flow cell was introduced more than 30 years ago,^[3] and several groups have made progress by improving efficiency *via* decreased hydrogen generation during charging;^[4-6] increasing iron plating density and efficiency;^[7] preventing precipitation of iron salts via complexation;^[8] and, manipulating the redox window through modification of the iron ligand present in solution.^[8] Many of the issues that are the focus of previous all-iron flow battery research are not a concern for the present concept because electrochemical charging does not occur. In essence, the present work is a re-optimization of the all-iron redox flow cell given a new set of goals and constraints set by the developing world product concept.

The critical electrochemical cell components are shown schematically in Figure 1, with the reactions:

The anode is iron metal, and the cathode is a carbon porous electrode (CPE). They are prevented from electronic short-circuit by a separator that allows ion transfer between the electrodes. The cathode active material is Fe^{3+} , present as an aqueous salt that flows through the CPE and reacts on its surface. Reactions (1) and (2) are the desired electrochemical reactions during discharge, and are accompanied by sulfate transport through the separator. Reaction (3) is the total desired reaction, a sum of Reactions (1) and (2). This reaction may also occur, however, by chemical disproportionation reduction of Fe^{3+} in contact with Fe^0 arising from crossover of Fe^{3+} through the membrane to the iron metal electrode surface. Essentially, crossover Fe^{3+} etches the metallic iron electrode rather than contribute to the desired electrochemical reaction. Thus, Fe^{3+} crossover through the membrane introduces self-discharge inefficiency, and should be minimized.

2.0 Experimental methods

Electrolyte solutions were prepared by mixing de-ionized water with FeCl_3 (Sigma-Aldrich), $\text{Fe}_2(\text{SO}_4)_3$ (Sigma Aldrich), NaCl (BDH), or Na_2SO_4 (Alfa-Aesar). Low-carbon steel and cast iron sheets were provided by McMaster-Carr. Note both sheets were cleaned with acetone and polished lightly with sand paper before cell assembly to eliminate surface oxidation or machine oil contamination. Porous iron was prepared by sintering a loosely-packed bed of pure iron particles at 800°C in argon. Carbon porous electrode papers were provided by Freudenberg (H2315), SGL (Sigracet 10AA), or Mitsubishi Rayon Co. Ltd (MRC U105).

Solution conductivity and pH were measured with an Orion Star A325 meter. Viscosity was measured with a Brookfield DVII+ Pro viscometer and CP-42 cone.

Cells were assembled in standard fuel-cell-testing hardware (Fuel Cell Technologies) with 10 cm^2 active area. The carbon porous electrode and iron electrode were inserted in window-frame shape Teflon

gaskets, the thickness of which was selected to compress the carbon porous electrode to about 80% of its free-standing thickness. The iron thickness (at least 0.15 mm) was selected to be significantly thicker than necessary, so that consumption of iron metal did not limit cell capacity. Electrolyte solution was provided by a peristaltic pump at 60 mL min^{-1} , and was recirculated continuously through the cell. Polarization behavior was assessed with 60 mL solution volume to minimize state-of-charge (SOC) variation during the experiment. Experiments where the electrolyte solution was discharged fully used 15 mL solution volume to mimic the expected use case of 1 to 2 h discharge time. Cells were tested with a VMP-3 (BioLogic) potentiostat with electrochemical impedance spectroscopy capability. Polarization curves were obtained by recording the voltage at the end of 10 sec long current steps, which were found to be long enough to ensure pseudo steady-state. Constant-current discharge utilized a voltage limit of 0 V to ensure maximum discharge energy. Constant-voltage discharge utilized a current limit of 2 mA cm^{-2} .

Results and Discussion

1. Iron solution characterization

Solutions of $\text{Fe}_2(\text{SO}_4)_3$ and FeCl_3 were prepared in the concentration range 0.25 to 2 M. Conductivity, pH and viscosity of these solutions is shown in Figure 2. As is typical for simple salt solutions, conductivity initially increases with molarity due to increasing concentration of charge carriers, then peaks and decreases due to increased solution viscosity and therefore reduced ion mobility. Conductivity of the sulfate solutions is significantly lower than for chloride solutions, and this was stated as the basis for selecting the iron chloride system as the focus of early work with the all-iron battery.^[3] Viscosity increases roughly linearly in the concentration range studied, which is a concern for the simple system addressed here, as increased viscosity will increase the requirement for continuous mechanical pumping energy (delivered by hand) or tank and cell pressure if the system is pressurized only at the beginning of the discharge run. If the solution is gravity fed, high viscosity will reduce the flowrate through the (+) CPE. Upon discharge, solution concentration increases as iron is stripped from the (–) metal electrode due to Reaction 2. For example, 0.5 M $\text{Fe}_2(\text{SO}_4)_3$ (23 mS cm^{-1} conductivity, 1.2 cP viscosity, and 1.6 pH) will

discharge completely to 1.5 M FeSO_4 (66 mS cm^{-1} conductivity, 2.8 cP viscosity, and 2.8 pH). Thus, discharge causes a moderate increase in conductivity, viscosity, and pH.

The native pH of these solutions is quite low. Fortuitously, the operating pH window is well below pH 3.5. Above that value, the iron salts convert to iron hydroxide, a low-solubility salt that tends to precipitate out of solution. During electrochemical charging of the conventional all-iron battery, pH can rise above this limit, and buffering, addition of ligands, or other measures must be taken to avoid precipitation.^[8] The design choice of limiting the present system to only discharge eliminates this complication.

In the rechargeable all-iron cell, the typical iron salt is FeCl_3 , chosen for its high solubility and conductivity in aqueous solution.^[3,8] In this work, we must also account for the potential for negative human and environmental health impacts. Iron sulfate is a source of iron used in dietary supplements, and is used in dentistry and wastewater clean-up. In contrast, FeCl_3 is a chemical etchant and suspected to be harmful to aquatic life. The cost for each is less than US\$300 per ton. Based on these considerations, the focus of this work is determining and improving performance using the more benign iron sulfate. We do, however, include some results with iron chloride for comparison.

2. Separator screening and selection

A wide range of commercially-available anion exchange membranes (AEM), proton exchange membranes (PEM), microporous separators, and papers were screened for open-circuit voltage (OCV) and initial performance. Most candidates were removed from further consideration due to low OCV or poor initial discharge performance. Polarization is shown for the three remaining candidates with both 0.5 M $\text{Fe}_2(\text{SO}_4)_3$ and 1 M FeCl_3 in Figure 3. The different salt molarities are chosen to make a comparison between solutions with the same Fe^{3+} ion concentration. The anion exchange membrane (Ameridia AMX)

shows the highest OCV (close to that predicted by Eq. 3), whereas the others have OCV significantly below the theoretical value. This is probably due to high crossover which causes self-discharge and concomitant deviation from the standard potential at the iron metal anode as shown in Figure 1. The flux of Fe^{2+} back to the cathode may also reduce the potential due to Nernstian effects. Despite the high OCV for AMX, the slope of the polarization curve, which is indicative of the area-specific resistance (ASR) limits the peak power. Paper also displays a roughly linear polarization curve, but has significantly lower resistance. In contrast, Daramic has limiting current behavior, which limits peak power in the case of $\text{Fe}_2(\text{SO}_4)_3$. We surmise the limiting current arises from mass transport limitation in the membrane, as the high current density achieved for paper indicates mass transport in the (+) electrode is sufficient. Note that the Daramic membrane is roughly 3 times thicker than the paper compared in Figure 3. The limiting current for $\text{Fe}_2(\text{SO}_4)_3$ is significantly lower than for FeCl_3 . This comparison highlights that the design goal of eliminating health and environmental risk also means accepting the lower performance of the sulfate salt.

Peak power density is shown for paper, AMX, and Daramic membranes as a function of $\text{Fe}_2(\text{SO}_4)_3$ concentration in Figure 4. The peak power generally decreases with increasing concentration due to the viscosity and conductivity trends shown in Figure 3. Note that AMX is significantly more expensive than Daramic and paper, and provides no performance benefit. It was therefore eliminated from further consideration.

Various types of office paper were tested, including different colors, thicknesses, and surface finishes. One clear trend is that performance depends on paper thickness, as shown in Figure 5. All papers provided relatively linear discharge polarization curves, but thicker paper produced much higher area-specific resistance (ASR). Peak power density and ohmic impedance are correlated to paper thickness in Figure 5, and the results are consistent with ohmic loss in the membrane dominating cell performance for the case of paper. There is some scatter in the correlation, suggesting a secondary influence in addition to

thickness. We did note that solution conductivity increased after wetting the paper in the solution, and the magnitude of this effect varied significantly between the various paper types. Presumably this arises from paper-making additives dissolving or affecting solution pH. We did not study this phenomenon systematically, as the intentional addition of supporting electrolyte had a much larger impact on cell performance as discussed below in Section 3.

3. Supporting electrolyte

The impact of paper thickness and the observation of higher performance for FeCl_3 , which has much higher conductivity than $\text{Fe}_2(\text{SO}_4)_3$, suggests that ohmic losses in the solution phase dominate cell performance. We therefore increased solution conductivity via addition of supporting electrolyte salts, as shown in Figure 6a. This also increases the limiting current, as the supporting electrolyte introduces charge carriers that are not involved in the reactions and therefore are not diffusion limited across the separator at the low limiting currents observed in Figure 3. Na_2SO_4 and NaCl were chosen because they are easily soluble, inexpensive, and benign. The rate of increase of solution conductivity with increasing supporting electrolyte concentration is similar for both salts, and the solutions with FeCl_3 remain consistently higher than with $\text{Fe}_2(\text{SO}_4)_3$. Note that higher concentrations of NaCl are achievable due to the solubility limits of 6.1 M for NaCl and 1.5 M for Na_2SO_4 .

The impact of supporting-electrolyte concentration on peak power density for cells with paper and Daramic separators is shown in Figure 6b-c. The general trend is that increasing supporting electrolyte salt concentration initially increases cell power due to increased conductivity. The cell power peaks and declines at higher concentration as mass-transport limitations begin to restrict peak power. Polarization curves are compared for 1.2 M addition of supporting electrolyte in Figure 6d. A maximum peak power of roughly 75 mW cm^{-2} is achieved for 0.5 M $\text{Fe}_2(\text{SO}_4)_3$ *via* addition of 1.2 M NaCl , which compares favorably to the power density in the range of 20 to 50 mW cm^{-2} reported previously for the all-iron battery.^[3,9] This electrolyte formulation is used to characterize discharge behavior of the cell, below.

4. Electrode effects

Various types of (+) CPE and (–) iron metal electrode were tested to assess the impact of each electrode on cell performance, and evaluate the potential of electrode optimization to increase cell performance. The effect of CPE type is show in Figure 7. The primary impact is on discharge polarization slope (ASR). The 10AA and H2315 performed significantly better than MRC U105.

Figure 8 compares discharge polarization curves for various (–) iron-metal electrode types. For the dense sheet types, commercial-grade gray cast iron (96% Fe) and low-carbon steel (98.5% Fe) were used because they are widely available and less expensive than high-purity iron, and thus well-suited to use as a low-cost disposable electrode. The primary alloying elements for both types are C, Mn, and Si. Low carbon steel provided the best performance, possibly due to the higher iron content, or favorable kinetics arising from grain structure or other metallurgical properties. A 2 mm thick porous coupon of sintered pure iron particles provided similar polarization to dense cast iron, suggesting that surface area for iron oxidation (Reaction 2) does not limit performance. The impact of the iron-metal electrode type was much smaller than the impact of (+) CPE discussed above. Low carbon steel was selected for all experiments described below.

5. Discharge behavior

When the cell is discharged, Fe^{3+} at the (+) electrode and Fe^0 at the (–) electrode are both converted to Fe^{2+} , decreasing the Fe^{3+} concentration, but increasing the total iron concentration in solution. This reduces the potential and leads to changes in solution properties. Upon complete discharge a solution of 0.5 M $\text{Fe}_2(\text{SO}_4)_3$ with 1.2M NaCl (60 mS cm^{-1} conductivity, 2.8 cP viscosity, and 1.8 pH) becomes 0.75 M FeSO_4 with 1.2M NaCl (63 mS cm^{-1} , 3.0 cP, 2.5 pH). Furthermore, as the (–) electrode is consumed,

cell compression and (+) electrode thickness may change, and gaps may form at the separator/(-) electrode interface. For these reasons, cell performance is not expected to remain constant as the state of charge (SOC) decreases during continuous discharge. Figure 9 shows how performance evolves as a function of SOC. The OCV for paper separator is always lower than for Daramic, likely arising from higher crossover of Fe^{3+} through the thinner paper. The ASR slope of the discharge curves increases as Fe^{3+} is consumed, presumably due to both decreased reactant concentration and increased solution viscosity. The overall result is that peak power declines dramatically as discharge proceeds. The paper separator produced higher power than Daramic at all SOC, so it was selected for use in the experiments discussed below.

Cells were discharged at various current densities and voltages to optimize the total energy extracted from the consumable materials. Note that excess iron metal was used at the (-) electrode so theoretical capacity is limited by Fe^{3+} . Selected constant-current discharges are shown in Figure 10a. At high current density (75 mA cm^{-2}), polarization losses lead to low output voltage and curtail the capacity. At low current density (12.5 mA cm^{-2}), voltage remains high over the entire discharge and the sharp change of the curve at the end of discharge suggests complete consumption of the Fe^{3+} . At such low operating current, however, the self-discharge current becomes a significant source of inefficiency, and consumes a large portion of the Fe^{3+} , leading to low utilization. We suspect self-discharge is reduced at low SOC, where the concentration of Fe^{3+} is lower. At intermediate current density (37.5 mA cm^{-2}), voltage remains relatively high and utilization is improved. A typical constant-voltage discharge is shown in Figure 10b. Initially, the current decreases rapidly presumably due to both ASR and mass transport effects (see Figure 9a), but then remains between 30 and 50 mA cm^{-2} throughout most of the discharge period, and finally drops rapidly at the end of discharge. Again, Fe^{3+} utilization is less than 100% due to self-discharge. The images inset to Figure 10b show the color of the solution in the reservoir (a clear plastic vial). The color remains brown until about 90% of the capacity is utilized, and then quickly changes to faint blue. This provides a

clear visual indication to the end-user that all Fe^{3+} in the solution is consumed, and another batch of fresh solution is required to generate more energy. The surface of the iron metal is heavily pitted after discharge, although this does not prevent it from being reused during subsequent discharge runs until it is consumed.

Figure 11 summarizes the impact of current density or voltage selection on average power, discharge energy, coulombic efficiency, and utilization of the consumable $\text{Fe}_2(\text{SO}_4)_3$. For constant-current operation (Fig. 11a), the average power increases rapidly with current density up to 25 mA cm^{-2} , above which power is constrained by low cell voltage (see Figure 10a). At 50 mA cm^{-2} and higher, energy is impacted by under-utilization of the Fe^{3+} , as described above. For constant-voltage operation (Fig. 11b), there is a broad maximum in power. Power drops as expected at very low voltage or very low current (which occurs at high voltage approaching the OCV). There is a broad maximum in energy for both constant-current and constant-voltage operation ranging from 12.5 to 37.5 mA cm^{-2} and 0.4 to 0.6 V . This makes the system forgiving of operating point variation, and suggests there is scope to implement more sophisticated control strategies, such as peak power tracking, to further optimize energy delivery.

Solution utilization refers to the fraction of Fe^{3+} used to produce power (as opposed to being consumed by self-discharge, or remaining in solution after cell voltage reached the cutoff of 0 V in the case of constant current), and is taken as the ratio of discharge capacity to the theoretical solution capacity (26.8 Ah L^{-1} for $0.5 \text{ M Fe}_2(\text{SO}_4)_3$). Utilization is reduced at high current density, at which the lower voltage limit is engaged before all of the Fe^{3+} is consumed (see Fig 10a). This effect is not seen at low voltage, as current is allowed to decay until all Fe^{3+} is consumed. Coulombic efficiency of Fe^{3+} consumption can be calculated as the ratio of useful discharge capacity to total discharge capacity (*via* both useful discharge and self-discharge). Total discharge capacity is easily determined by weight loss of the iron metal (expressed as mAh theoretical equivalent). Corrosion was ruled out as a significant contributor to metal consumption by soaking an iron block in the electrolyte solution and finding a corrosion rate of roughly

0.8 mA cm⁻². Therefore, the inefficiency is ascribed entirely to self-discharge. Self-discharge current was thus estimated to be 7 to 11 mA cm⁻² for most discharge runs and severely limits coulombic efficiency, and therefore utilization, at low current density/high voltage.

A practical goal is to maximize energy obtained from the consumable materials. From this standpoint, 25 mA cm⁻² is the optimum discharge current under constant-current conditions. Energy is constrained by self-discharge at lower current density and cell ASR at higher current density. Separator properties such as thickness, porosity, and permeability impact both limitations, so further separator optimization may lead to improved power. It is anticipated, however, that there is a trade-off between crossover and ohmic resistance when optimizing the membrane, as seen in the Br₂-H₂ redox flow system for which crossover is also a significant limitation at low current density/high voltage.^[10] It is also desirable to improve reaction kinetics if they contribute significantly to cell ASR. In fact, the (–) electrode was previously found to be the largest source of voltage loss during discharge for an all-iron cell with high-conductivity electrolyte.^[3] The (+) electrode kinetics are not expected to limit cell performance, as current density an order of magnitude higher is achieved in the iron-hydrogen flow cell with similar electrolyte solution and (+) electrode material.^[11] Therefore, further electrode optimization effort should focus on the (–) electrode.

6. Practicality and cost

The performance results discussed above can be used to assess the practicality and costs of using the all-iron cell as a primary battery with re-charge accomplished by replacing the consumable chemical reactants. Although it is expected that further improvements to performance and efficiency are possible, it is worthwhile to assess the feasibility of this system for the proposed application with the data available. Table 1 shows the design scenario based on the performance at 0.55 V shown in Figure 11b, and a target

of providing the end-user with 5.4 Wh during a single discharge run, enabling recharging of a mobile phone battery.

The cell size and solution volume are reasonable, enabling a small, handheld device. At the 0.5 M $\text{Fe}_2(\text{SO}_4)_3$ concentration used in Section 5, the user would have to mix the consumable chemicals with water to a final volume of 470 mL. Note that decreasing solution concentration below 0.23 M $\text{Fe}_2(\text{SO}_4)_3$ would result in more than 1 L of water being consumed; this is prohibitive for individuals without easy access to clean water supply. Although it may be desirable to reduce solution concentration to decrease self-discharge, this consideration presents a practical limit. It is worth noting that replacing deionized water with domestic tap water or local creek water (Strawberry Creek, Berkeley, CA USA) reduced cell performance slightly in the case of unsupported solutions, and had minimal impact in the case of solutions with supporting electrolyte. The impact of low water quality found throughout the developing world on cell performance should be addressed in the future. Assuming the power density achieved here is not reduced when scaling up cell size, a cell area of 150 cm² (about the size of the human hand) is required to meet the design target. It is expected that the total cell area will be broken down into several smaller cells connected in series to provide the 5V required by the prevalent USB battery charging standard.^[12] Thus, a stack of smaller individual pieces of (+) CPE, separator, and iron foil (–) electrode will be provided for the user to insert into the cell housing. We have found that it is desirable to replace the paper separator after a single complete discharge, as the wet paper tends to be damaged upon cell disassembly. In contrast, with careful handling the carbon paper CPE can be reused. At US\$80 m⁻²,^[13] the CPE will cost US\$1.20. This is expected to be a significant fraction of the total device cost, which would also include an inexpensive plastic housing, metal electrical contacts, and jack for the phone charging plug. Further increasing power density to reduce the cell area requirement could therefore significantly reduce the total cost of the device to the end user.

Table 2 shows the amount of consumables required per discharge run. The volume of consumables is small and is dominated by the salts, which could easily be provided as a single-use packet or tablet about half the size of a deck of cards. The consumables cost for a discharge run is US\$0.034 (\$6.45 kWh⁻¹), which compares very favorably to kiosk-based mobile phone charging (\$0.25 per charge). Iron sulfate dominates the consumables cost so further cost reductions could be achieved by increasing the Fe³⁺ utilization. At the optimum current and voltage, the utilization is dominated by coulombic inefficiency which could be improved either by increasing the rate of the desired reactions, or decreasing the self-discharge rate.

Conclusions

An iron-based redox flow battery was developed and optimized for use as a consumer device for off-grid portable power generation. The constraints of low-cost and non-toxic materials coupled with the concept of the end-user recharging the cell manually by replacing consumable materials led to a different materials set and design solution than previous work on the all-iron battery system. Fe₂(SO₄)₃ was chosen as the active material for human and environmental health concerns, although this reduces cell performance compared to FeCl₃. Extremely inexpensive separator materials including office paper and microporous membrane were found to be suitable. Adding supporting electrolyte to the Fe₂(SO₄)₃ solution dramatically increased performance. There is significant scope for future improvements to the cell performance by further optimizing the Fe₂(SO₄)₃ and supporting electrolyte concentration, identifying improved CPE materials and structures, and decreasing the impact of self-discharge possibly via separator selection. At the observed power and energy metrics, the cell design is practical in terms of cell size, amount of consumables, volume of water required, and costs, and worth further exploration.

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Figure Captions

Figure 1. Schematic of cell during discharge. The desired electricity producing reactions, and undesired self-discharge (iron disproportionation) reactions are indicated.

Figure 2. (a) Conductivity, (b) viscosity, and (c) pH of aqueous $\text{Fe}_2(\text{SO}_4)_3$ (circles) and FeCl_3 (squares).

Figure 3. Effect of membrane on performance with (a) 1 M FeCl_3 or (b) 0.5 M $\text{Fe}_2(\text{SO}_4)_3$. Membrane types: AMX (squares), Daramic (triangles), printer paper (circles).

Figure 4. Effect of concentration on performance with 0.5 M $\text{Fe}_2(\text{SO}_4)_3$. Membrane types: AMX (squares), Daramic (triangles), office paper (circles).

Figure 5. Effect of paper separator thickness on power density (squares) and ohmic impedance (circles) with 0.25 M $\text{Fe}_2(\text{SO}_4)_3$.

Figure 6. Effect of supporting electrolyte concentration for solutions with 0.5 M $\text{Fe}_2(\text{SO}_4)_3$ (circles) and 0.5 M FeCl_3 (squares) with additional supporting electrolyte salt: NaCl (closed symbols) or Na_2SO_4 (open symbols). (a) Solution conductivity, (b) peak power with paper separator, (c) peak power with Daramic separator, and (d) Performance with paper separator.

Figure 7. Comparison of various (+) CPE materials with Daramic separator and 0.5 M $\text{Fe}_2(\text{SO}_4)_3$ solution. Sigracet 10AA (open squares), Fruedenberg H2315 (open triangles), MRC U105 with PTFE loading of 0% (closed squares).

Figure 8. Comparison of various (–) iron-metal electrode types with paper separator and 0.2 M $\text{Fe}_2(\text{SO}_4)_3$ + 3 M NaCl solution. Low carbon steel sheet (squares), gray cast iron sheet (circles), and sintered porous iron (triangles).

Figure 9. Effect of state of charge (SOC) on performance with (a) paper separator or (b) Daramic separator. SOC is labeled in the figure (fully charged = 1.0).

Figure 10. Discharge of 0.5 M $\text{Fe}_2(\text{SO}_4)_3$ + 1.2 M NaCl solution with paper separator under conditions of: (a) constant-current, with current density labeled in the graph, or (b) constant-voltage (0.55V). Images of the solution at various points along the constant-voltage discharge curve are inset to show the color change.

Figure 11. Performance metrics determined from (a) constant-current or (b) constant-voltage discharges such as those shown in Figure 10 with 0.5 M $\text{Fe}_2(\text{SO}_4)_3$ + 1.2M NaCl solution and paper separator.

Discharge energy (E, triangles), average power density (P, diamonds), coulombic efficiency (η , squares), and Fe^{3+} utilization (U, circles) are shown.

Table captions

Table 1. Design scenario for mobile feature-phone charging, assuming 0.65 Ah phone battery charged at 5 V, through power conditioning circuit that transfers charge from iron battery to phone battery at 60% efficiency.

Table 2. Consumables required for each mobile phone charging session.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Table 1

<u>Observed Performance</u>		<u>Discharge Requirements</u>			<u>Size of Device</u>	
Energy Density (Wh/L)	Power Density (mW/cm ²)	Energy (Wh)	Discharge Time (h)	Power (W)	Solution	
					Volume (mL)	Cell Area (cm ²)
11.5	18	5.4	2	2.7	470	150

Table 2

	Iron Sulfate	Sodium Chloride	Iron Foil	Office Paper	TOTAL
Weight (g)	94	14	16	0.9	125
Volume (cm ³)	30.3	6.5	2.0	1.5	40
Cost (US\$)	0.023	0.001	0.008	0.002	0.034

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