A High Efficiency Iron-Chloride Redox Flow Battery for Large-Scale Energy Storage

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We report advances on a novel membrane-based iron-chloride redox flow rechargeable battery that is based on inexpensive, earth-abundant, and eco-friendly materials. The development and large-scale commercialization of such an iron-chloride flow battery technology has been hindered hitherto by low charging efficiency resulting from parasitic hydrogen evolution at the negative electrode and high overpotential losses. We have demonstrated a high charging efficiency of 97% by maintaining the negative electrolyte at a pH value of 2 and by using indium chloride as an electrolyte additive. The high charging efficiency of the negative electrode was found to be stable over at least 50 cycles. Further, we have demonstrated that with a graphite felt electrode, the overpotential losses were substantially mitigated at the positive and negative electrodes allowing the electrodes to be operated at current densities as high as 100 mA/cm². Within these technical advancements, the iron-chloride redox flow battery has an increased prospect of being a sustainable and efficient solution for large-scale energy storage.

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Large-scale energy storage systems that are inexpensive, robust, and highly efficient are essential for the integration of renewable energy sources like solar and wind into the electrical power grid. Rechargeable batteries are particularly promising for such grid-scale applications because of their efficiency, modularity, and flexibility to siting.1–4 Several battery systems including lithium-ion, lead-acid, sodium-sulfur, and the all-vanadium redox flow battery have been deployed at the mega-watthour scale.5–8 However, the levelized cost of energy delivered (LCOE) for these state-of-art battery systems is about ten to fifty times higher than the target values identified by the U.S. Department of Energy (DoE).9–11 In addition, the aforementioned battery systems pose challenges from the standpoint of sustainability and environmental friendliness because of the relatively expensive and toxic materials used. Therefore, the development of high-performance and long-life batteries that use inexpensive, eco-friendly, and abundantly-available materials is an important topic of current research.

Redox flow batteries for large-scale energy storage.—Redox flow batteries are particularly well-suited for large-scale energy storage applications.5,12–16 Unlike conventional battery systems, in a redox flow battery, the positive and negative electroactive species are stored in tanks external to the cell stack. Therefore, the energy storage capability and power output of a flow battery can be varied independently to suit the desired application. For example, if an application requires a battery with high energy content, the amount of electroactive species in the tanks can be increased without significant modification to the cell stack. As the electroactive material is held in the external tanks, an increase in the amount of electroactive species does not require an increase in the volume of the cell stack. Thus, modifications to the battery design for increased energy output can be realized at minimal cost and without any impact on the power output of the system. In contrast, any attempt to increase the energy content of a conventional battery often results in a significant increase in the system cost if the specific power has to be maintained.

Among the various redox flow battery chemistries that have been studied, the all-vanadium redox flow battery has seen the widest commercial deployment. Systems as large as 250 kWh to 1 MWh have been demonstrated.17 Since the all-vanadium redox flow battery uses just vanadium redox-active species in the positive and negative electrolyte, any electrolyte cross-over or capacity imbalance that occurs during operation can be addressed by appropriate electrolyte re-balancing external to the cells. However, the high cost, limited earth-abundance, and the relatively high toxicity of vanadium present challenges to the widespread adoption of vanadium-based batteries.

Similar to the all-vanadium system, the iron-chromium redox flow battery also uses fully soluble redox species in both the positive and negative electrolytes.18 However, preventing crossover of materials from one electrode compartment to the other requires special membranes.19 While significant progress has occurred in the last five years in the deployment of the iron-chromium redox flow battery, the low natural-abundance of chromium, and the poor kinetics of the chromium electrode would be barriers for large-scale use.20 Flow-battery systems based on zinc-bromine and iron-chloride chemistries are considered “hybrid” redox flow systems as metal deposition occurs from a solution of metal ions at the negative electrode, while the positive electrode operates on a redox couple that is soluble in both the oxidized and reduced forms.21 Our interest focuses on the iron-chloride flow battery (also referred to as the “all-iron” battery) that relies on the use of iron-based materials at both electrodes. With the abundant earth resources of iron and chloride, this type of battery is particularly attractive for large-scale applications.

Operating principle of an iron-chloride redox flow battery.—A schematic of the principle of operation of this system is shown in Figure 1. The redox chemistry of the iron-chloride redox flow battery is based on the iron (II) chloride/iron (III) chloride couple at the positive electrode and the iron (II) chloride/metallurgical iron couple at the negative electrode. The reactions that take place during the charging and discharging of an iron-chloride redox flow battery are shown schematically in Figure 1 and in the following chemical equations.

Positive electrode : $2\text{FeCl}_3 + 2\text{e}^- \rightleftharpoons 2\text{FeCl}_2 + 2\text{Cl}^- \quad E^0 = 0.77 \text{ V}$

[1]

Negative electrode : $\text{Fe} + 2\text{Cl}^- \rightleftharpoons \text{FeCl}_2 + 2\text{e}^- \quad E^0 = -0.44 \text{ V}$

[2]

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The open-circuit voltage of the iron-chloride redox flow battery is iron (II) chloride at the positive electrode. At the negative electrode, in the resistance of the separator due to the precipitation of iron, the energy efficiency observed was 50%. They also observed an increase in the performance of an all-iron redox flow cell with titanium and carbon electrodes. The authors have also re-affirmed that the iron-chloride redox flow battery has long life, is eco-friendly and uses raw materials that are inexpensive.22

Thus, elemental iron is thermodynamically unstable under such conditions and hydrogen would evolve even at open circuit. Such corrosion of iron in acidic media accompanied by the hydrogen evolution reaction is well known.24 Further, during charging of the iron-chloride redox flow battery, the electro-deposition of iron presents substantial overpotential thereby facilitating the hydrogen evolution reaction further. Thus, a significant amount of the input charge is directed towards hydrogen evolution resulting in a low charging efficiency. In addition, the evolution of hydrogen also results in an increase in the pH of the negative electrolyte. If the pH of the negative electrolyte increases beyond 3, precipitation of iron (III) and iron (II) hydroxides would occur. Maintaining the pH of the negative electrolyte below 3 is essential to the stable long-term performance of the iron-chloride redox flow battery. Thus, to achieve stable operation and high round-trip energy efficiency it is imperative that the charging efficiency at the negative electrode be close to 100%.

Approaches to suppress hydrogen evolution.—The rate of hydrogen evolution during charging is dependent upon the concentration of hydronium ions in the negative electrolyte. The natural pH of a 3 M solution of iron (II) chloride tetrahydrate is in the range of 0.7 – 1.0. This low pH value facilitates the evolution of hydrogen during charging. We have focused on inhibiting the hydrogen evolution reaction by two approaches: (1) introducing limitations to the transport of hydronium ions to the electrode surface, and (2) inhibiting the kinetics of the charge-transfer process that leads to the evolution of hydrogen. Recently, Savinell et al. have reported the effect of supporting electrolyte type and electrolyte pH on the rate of hydrogen evolution on iron electrodes.25 As the electrolyte pH was increased from 1 to 3, the hydrogen evolution current was observed to decrease from 15 mA/cm² to 0.7 mA/cm² at ~0.8 V (vs Ag/AgCl). Also, the hydrogen evolution current density was reported to be much lower in a chloride-based electrolyte compared to an electrolyte based on the sulfate anion. The highest faradaic efficiency of iron deposition on copper of 97% was observed in a sodium chloride electrolyte.25

Advantages of the membrane-based system.—Our configuration of the iron-chloride redox flow battery uses an anion-exchange membrane separator between the two electrode compartments. This configuration has several advantages compared to that of the porous-separator-based cell configuration reported in the literature.21 The membrane-based configuration prevents the crossover of reactants between the positive and negative electrode compartments. Loss in charging efficiency of the negative electrode due to any ferric ion that crosses over from the positive electrolyte is completely avoided. Also, the anion-exchange membrane separator allows different pH values to be maintained on each side of the cell. In the porous-separator-based cell design, the facile crossover of the electrolyte equalizes the pH in the two compartments leading to undesirable consequences. For instance, in the porous-separator-based design, the need to maintain the pH of the negative electrolyte around 2 (to suppress hydrogen evolution) requires the positive electrolyte to be kept around this pH value as well. At this pH, the ferric ions in the positive electrolyte will start forming hydroxide precipitates. To prevent the precipitation of these iron hydroxides, complexing agents are added to the positive electrolyte. While such complexing agents improve the solubility of the ferric ions, they can potentially hinder the kinetics of charge transfer for the positive electrode reaction. Further, the cross-over of these complexing agents to the negative electrolyte through the porous separator could have unintended consequences. A recent report from Prof. Savinell’s group has documented the effect of various chelating ligands on preventing the precipitation of hydroxides in the positive electrolyte.22 The effect of various ligands on the electrochemical and transport properties of the ferric/ferrous positive electrode couple has been studied. Among the various additives studied, glycine was found to inhibit the precipitation of iron (III) without significantly altering the diffusion coefficient and electrochemical characteristics of the ferrous/ferric couple.26 However, the glycine additive was observed to decrease the plating efficiency of the negative electrode indicating the challenges of using a porous-separator-based flow cell design.25,26

One of the disadvantages in the use of an anion-exchange membrane is the need for such a membrane to have adequate conductivity.
for the anion that is transferred – in this case, the chloride ion. Among other challenges are the stability of the membrane in acidic and oxidative environments, and the added cost of the membrane. Therefore, a thin, mechanically-robust, and inexpensive membrane with low ionic resistance and high chemical durability will be required.

Experimental

Measurements of the faradaic efficiency for the electro-deposition of iron in various electrolytes were conducted using a three-electrode “half-cell” with a rotating disk glassy carbon working electrode. The effect of additives and electrolyte pH on the charge/discharge performance of an iron-chloride redox flow battery was studied in a “full-cell” with electrolyte flowing across two electrodes separated by an anion-exchange membrane.

Faradaic efficiency of iron deposition.— The half-cell set up consisted of a glassy carbon rotating disk working electrode (RDE) (Pine Instruments), a silver/silver chloride (Ag/AgCl) reference electrode and a platinum wire counter electrode. The electrolyte was an aqueous solution of iron (II) chloride tetrahydrate (3 moles liter⁻¹) with ammonium chloride (2 moles liter⁻¹), the latter serving to increase the conductivity of the solution. Experiments were conducted with various electrolyte additives that included ascorbic acid, citric acid, indium chloride, or bismuth oxychloride. The concentration of each of these additives in the electrolyte has been indicated along with the performance results. During preparation and electrochemical testing, the electrolyte was de-aerated and a blanket of argon gas was maintained to prevent the oxidation of ferrous ions to ferric ions. The glassy carbon electrode was rotated at 2500 rpm in all the measurements to provide adequate mass transport of the ferrous ions. The experiments with the half-cell were performed using a PAR VMC-4 potentiostat. The faradaic efficiency of electro-deposition of iron was determined by plating iron on to the glassy carbon RDE at various values of current density in the range of 10–300 mA/cm² followed by anodic stripping of the iron deposit at 60 mA/cm². The stripping current density was determined from the ratio of the charge delivered during the stripping step to the charge deposition and stripping of iron on the glassy carbon RDE is an example of the potential-charge curves measured during the constant current deposition and stripping of iron on the glassy carbon RDE.

Correction of electrode potentials for ohmic drop.— The electrode potentials measured during the charging and discharging of the iron-chloride redox flow cell were corrected for the voltage drop across the series equivalent ohmic resistance. The impedance of the positive electrode and negative electrode was measured in a three-electrode configuration as a function of the frequency of the alternating current excitation signal. For this measurement, the working electrode lead of the potentiostat was connected to the electrode of interest, the reference electrode lead was connected to the silver/silver chloride reference electrode in the same electrode compartment, and the counter electrode lead was connected to the opposite electrode (positive or negative). The high-frequency intercept of the impedance on the complex-plane plot was noted as the series equivalent ohmic resistance.

Results and Discussion

Faradaic efficiency for the electro-deposition of iron.— An example of the potential-charge curves measured during the constant current deposition and stripping of iron on the glassy carbon RDE is shown in Figure 4.

The faradaic efficiency of iron deposition is calculated from the ratio of the charge delivered during the stripping step to the charge.
Further, complexation by ascorbic acid is also used in the nutrition industry to enhance the bio-availability of iron.26,29

In the presence of ascorbic acid or citric acid, the pH of the electrolyte could be increased to 2 by adding ammonium hydroxide without any precipitation of Fe²⁺ or Fe³⁺ hydroxides. The faradaic efficiency of iron deposition using this modified electrolyte (3 M iron(II) chloride tetrahydrate + 2 M ammonium chloride + 0.3 M ascorbic acid) at pH 2 was greater than 95% (Figure 5). The amount of ascorbic acid was chosen to be 0.3 M based on the minimum amount required for ensuring complete solubility of iron (II) chloride in the negative electrolyte. Similar high faradaic efficiencies were also observed when citric acid was used as the stabilizing agent (Figure 5). Ascorbic acid and citric acid with their pKₐ values in the range of 3.1 to 4.2 provide some buffering action, preventing rapid changes in the electrolyte pH during the electrodeposition and dissolution of iron.27

When depositing iron from the electrolyte containing ascorbic acid, the faradaic efficiency was about 90% at 10 mA/cm². The faradaic efficiency increased further with increasing current density reaching a value of 96% at 50 mA/cm². With further increase in the plating current density, the faradaic efficiency stayed constant; no further increase in efficiency was observed (Figure 5). Due to the relatively high pH of the electrolyte, the hydrogen evolution reaction was limited by the mass-transport of hydronium ions even at low values of plating current. The low concentration of protons in the bulk establishes a steep-gradient for proton transport to the electrode surface. With increasing total current density, the fraction of the current attributed to hydrogen evolution decreases because of the foregoing mass transport limitation. Thus, the fraction of the plating current diverted to the iron deposition reaction increased with increasing current density. However, as the deposition of iron from the ferrous ions in the electrolyte also became limited by mass transport, the partial current of iron deposition did not increase. Thus, the charging efficiency reached a constant value in the mass-transport-limited regime for both iron(II) and hydronium ions.

The maximum faradaic efficiency of iron deposition that can be obtained at a given concentration of iron (II) species and electrolyte pH can be estimated from the limiting currents for the iron deposition and hydrogen evolution reactions. The steady-state limiting current for iron deposition and hydrogen evolution can be related to the concentration from the Nernst diffusion layer model as,

\[ i_{\text{lim}} = nFDC^*/\delta \]  

Where \( i_{\text{lim}} \) is the limiting current density, \( n \) is the number of electrons involved in the reaction, \( F \) is the Faraday’s constant, \( D \) is the diffusivity of the electroactive species, \( C^* \) is the concentration of the species in the bulk of the electrolyte and \( \delta \) is the diffusion-layer thickness at the rotating disk electrode. The thickness of the diffusion layer at the rotating disk electrode during iron deposition can be calculated using the following expression.

\[ \delta = 1.61D^{1/3} \omega^{-1/2}v^{1/6} \]  

Where \( v \) and \( \omega \) are the kinematic viscosity of the electrolyte and the angular velocity of rotation, respectively. The diffusion coefficient for the H⁺ ion is 9.31 × 10⁻⁴ cm²/s and that of Fe²⁺ and Fe³⁺ is about 0.72 x 10⁻⁵ cm²/s;30 the kinematic viscosity of water is 10⁻² cm²/s. Using these parameters and the corresponding bulk concentration of protons and iron (II) ions in the electrolyte, the limiting current density for hydrogen evolution and iron deposition are 0.043 A/cm² and 4.67 A/cm², respectively. From the ratio of the limiting currents, the maximum efficiency of iron deposition for the electrolyte at a pH of 2 is calculated to be about 99%. This value of faradaic efficiency is consistent with the 96% efficiency observed in our experiments (Figure 5). Thus, we understand as to how an iron electrode operated at high current densities in electrolyte of pH~2 exhibits a high faradaic efficiency of iron deposition. However, operating the cell at such high current densities may not be feasible in the full-cell configuration both from a voltage efficiency standpoint and also due to the variable charging demands of a particular energy storage application. To overcome this challenge, we must inhibit the kinetics of charge-transfer

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**Figure 4.** Potential-charge curves measured during the deposition and stripping of iron on a glassy carbon RDE (rotation speed: 2500 rpm). Deposition and stripping experiments were performed at constant current density at the values indicated.

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**Figure 5.** Effect of complexing agents and electrolyte pH on the faradaic efficiency of iron deposition. Ascorbic acid and citric acid were at a concentration of 0.3 M.
for the hydrogen evolution reaction. To this end, we have studied the effect of indium chloride and bismuth oxychloride as additives to the negative electrolyte.

**Flow cell experiments – Effect of additives and electrolyte pH on charging efficiency.**—The potential-time curves measured during the charging efficiency measurement of the iron-chloride redox flow cell using a negative electrolyte containing ascorbic acid are shown in Figure 6. The measured charging efficiency on the negative electrode in the flow cell was consistent with the faradaic efficiency of iron electro-deposition measured in the half-cell testing (Figure 5). When the baseline negative electrolyte (3 M iron (II) chloride tetrahydrate + 2 M ammonium chloride) was used at its natural pH (0.9–1.0), the charging efficiency of the negative electrode was measured to be about 63% (Figure 7). In the presence of ascorbic acid and raising the electrolyte pH to 2 (with ammonium hydroxide), the charging efficiency increased to 83% (Figure 7). Based on the results from the half-cell experiments with a similar electrolyte, (Figure 5) the charging efficiency values are expected to be in the range of 80–90% at 20 mA/cm². Thus, the measured charging efficiency at the negative electrode in the flow cell was consistent with the results of half-cell measurements (Figures 5, 7).

Another approach to suppress hydrogen evolution on the negative electrode during charging is to increase the overpotential for hydrogen evolution. Indium and bismuth are known for their sluggish kinetics of hydrogen evolution. The exchange current densities for hydrogen evolution at the negative electrode during charging is to increase the overpotential for hydrogen evolution. Indium and bismuth are employed as electrolyte additives, the charge-transfer kinetics of hydrogen evolution can be expected to be inhibited in the same manner as with elemental indium or bismuth.

When indium chloride was present in the electrolyte (3 M iron (II) chloride tetrahydrate + 2 M ammonium chloride + 0.3 M ascorbic Acid, pH~0) at even a fairly small concentration of 0.2 mM, the charging efficiency increased to 83% (Figure 7). We restricted the amount of indium chloride to be small enough so that the limiting current density for the deposition of indium is <0.1% of that for the deposition of iron. When the pH of this indium chloride containing electrolyte was increased to 2, the charging efficiency of the negative electrode in the flow cell reached a value of 97%. From the half-cell studies (Figure 7), we observe that at the same current density, an indium-free electrolyte with pH~2 had a faradaic efficiency of only 86%. The increase in efficiency in the presence of indium chloride in the electrolyte results from the inhibition of the charge transfer process for hydrogen evolution in the presence of in situ electrodeposited indium metal. Therefore, the addition of indium chloride has enabled high charging efficiencies to be obtained even at low charging current densities – before mass-transport limitations set in.

When the negative electrode is charged in the presence of an electrolyte containing indium chloride, in addition to the reduction of iron (II) to metallic iron, the reduction of indium (III) ions to metallic indium also occurs. The standard reduction potential for the indium (III)/indium couple is –0.34 V. Thus, the deposition of indium can occur as the potential of the negative electrode during charging is sufficiently negative to the reversible potential of the In(III)/In couple (Figure 6). As discussed earlier, the deposited indium tends to be segregated and stays on the surface because of its immiscibility with iron. Even a monolayer of indium that stays on the surface of the iron is sufficient to hinder the kinetics of hydrogen evolution. This type of immiscibility is important to the success of this approach, as alloying will reduce the surface concentration of indium and the effective inhibition of hydrogen evolution.

In addition to indium, bismuth has been used as an additive for suppressing hydrogen evolution in alkaline zinc-, and iron-based batteries because of the high hydrogen overpotential on bismuth. Therefore, we investigated the effect of adding bismuth oxychloride to the electrolyte on the charging efficiency of the negative electrode. However, we observed that bismuth oxychloride did not have a noticeable impact on the charging efficiency of the negative electrode. We also noted that bismuth oxychloride was relatively insoluble in the negative electrolyte, unlike indium chloride. Thus, it is quite likely that we were not able to introduce sufficient concentration of bismuth ions into the electrolyte solution to have an impact on the hydrogen evolution reaction.

Given the high charging efficiency of 97% with indium chloride additive, the negative electrolyte with ascorbic acid and indium chloride at a pH of 2 was chosen for further studies. The specific composition of the negative electrolyte used in these studies was 3 M iron (II) chloride tetrahydrate, 2 M ammonium chloride, 0.3 M Ascorbic Acid, and 0.2 mM indium chloride at pH~2.

**Flow cell experiments- Effect of charging and discharging rate on efficiency.**—The charging efficiency of the negative electrode at different current densities of charge and discharge is shown in Figure 8. Consistent with the results of the half-cell experiments (Figure 5), the charging efficiency of the negative electrode showed an increase with increasing current density. The charging efficiency of the negative electrode also showed a lower value when the pH was ~0 instead of ~2.2. The charging efficiency reached a value as high as 97% at current densities as high as 40 mA/cm². The high charging efficiency observed even at 40 mA/cm² suggests that mass transport limitations in the flow cell may be reached at lower current densities than in the RDE experiment.

**Flow cell experiments- Optimization of the positive electrode.**—The redox transformation of the Fe²⁺/Fe³⁺ couple occurs at the positive electrode of the iron-chloride redox flow battery. During
charging, the oxidation of ferrous chloride to ferric chloride takes place; the reverse process occurs during discharge (Eq. 1). The kinetics of electron-transfer for the Fe$^{2+}$/Fe$^{3+}$ couple are facile and high rates can be sustained without significant activation overpotential. The standard exchange current density for the Fe$^{2+}$/Fe$^{3+}$ reaction has been measured to be about 1–5 mA/cm$^2$. Due to its facile and reversible kinetics, the Fe$^{2+}$/Fe$^{3+}$ reaction is a very attractive candidate as a positive electrode for redox flow batteries. The composition of the positive electrolyte used in this study was a mixture of 2 M iron (II) chloride tetrahydrate with 1 M iron (III) chloride and 2 M ammonium chloride in 1 M hydrochloric acid solution. When a graphite block was used as the current collector, the limiting current density on the positive electrode was 50 mA/cm$^2$ (diffusion layer thickness is about 0.3 mm) during charging and 30 mA/cm$^2$ during discharging. At 20 mA/cm$^2$ for example, the charging and discharging overpotentials were about 50 mV. In order to increase the current at the positive electrode, graphite felt (Sigracell) was used to pack the space between the graphite current collector and the membrane. The electrode of the performance was clearly seen in the polarization curves where the overpotential at high currents was found to be low (Figure 9). For example, both the cathodic and anodic overpotentials at 30 mA/cm$^2$ decreased by more than 50 mV after the addition of graphite felt to the positive electrode compartment. The polarization curves also did not exhibit any mass-transport limitation even at high current densities of charging and discharging. Current densities as high as 100 mA/cm$^2$ were achieved with a substantial decrease in effective current density expected to result from the use of the graphite felt. Modifications to the graphite felt (similar to that reported by Nguyen et al: growth of carbon nanotubes) will result in even greater area enhancements.

Further, the fluid flow field used in the full cell has not been optimized for the complete utilization of the active area of the graphite felt. Increasing the operating temperature will decrease the viscosity and also increase the diffusion coefficient facilitating mass transport in the diffusion layer. These modifications are expected to increase the limiting current density on both the positive and negative electrodes.

Flow cell studies - Charge/discharge cycling — The cell voltage-time curves measured during the charging and discharging of an iron-chloride redox flow cell are shown in Figure 10. The negative electrolyte of this iron-chloride flow cell consisted of 3 M iron (II) chloride tetrahydrate, 2 M ammonium chloride, 0.3 M Ascorbic Acid, and 0.2 mM indium chloride; the electrolyte pH was about 2.5. The positive electrode was packed with graphite felt and the electrolyte was a mixture of 2 M iron (II) chloride tetrahydrate with 1 M iron (III) chloride and 2 M ammonium chloride in 1 M hydrochloric acid solution. The use of an anion-exchange membrane allowed us to maintain different pH values on either side without the complication of cation crossover.

The cell voltage ($E_{cell}$) during charge and discharge was determined from the potentials of the positive and negative electrodes measured against the silver/silver chloride reference electrode in the respective compartments. The measured electrode potentials were corrected for all the voltage losses arising from series equivalent ohmic resistances at the electrodes. This arrangement also allowed us to ignore the significant voltage loss contribution across the membrane and electrolyte layers that were not part of the electrode. Thus, the charge-transfer and mass transfer polarization losses at the electrodes could be studied.

During charging, $E_{cell} = (E_p - \{I_{charge} \ast R_{Ω2,P}\})$
\[-(E_N + \{I_{charge} \ast R_{Ω2,N}\})\] [8]

During discharging, $E_{cell} = (E_p + \{I_{discharge} \ast R_{Ω2,P}\})$
\[-(E_N - \{I_{discharge} \ast R_{Ω2,N}\})\] [9]

Here, $E_p$ and $E_N$ are the measured potentials of the positive and negative electrodes, respectively. $R_{Ω2,P}$ and $R_{Ω2,N}$ are the ohmic resistances of the positive and negative electrode determined from the impedance data at high frequency. $I_{charge}$ and $I_{discharge}$ are the charging and discharging currents, respectively.

We observed that with increasing current density, the discharge voltage of the cell decreased (Figure 10). During discharge, we observed a well-defined plateau that corresponded to the dissolution of iron from the negative electrode. Once all the iron was stripped from
Figure 11. Voltage loss in the electrode and electrolyte layers at various charging and discharging current densities.

the electrode surface, the cell voltage dropped rapidly. The second plateau at low voltages during discharge at 10 mA/cm² could be due to the oxidation of iron (II) to iron (III) at the negative electrode. The cell voltage difference \(E_{\text{cell,charge}} - E_{\text{cell,discharge}}\) between charge and discharge is shown as a function of the operating current density in Figure 11.

Comparing the cell voltage losses with the changes in electrode potential at the negative electrode (Figures 12a, 12b), it is clear that 95% of the cell voltage losses could be attributed to processes at the negative electrode. At 10 mA/cm², the overpotential at the negative electrode is about 140 mV during charging and 100 mV during discharging – accounting almost entirely for the 250 mV voltage drop across the cell.

To verify the effect of mass transport and increased electrode area on the performance of the negative electrode, we changed the electrode configuration by including a graphite felt layer. With the graphite felt, the overpotential at the negative electrode decreased by almost 50% at all the current density values (Figure 13). While we had considered a planar electrode initially for the negative electrode, it appears that a porous electrode structure has significant benefits in reducing the overpotentials for the deposition and stripping of iron.

Flow cell studies - Stable operation of the cell during prolonged cycling.— Repeated cycling of the iron-chloride flow cell with the high-efficiency electrolyte at 40 mA/cm² demonstrated that a high charging efficiency (> 95%) could be maintained over 50 cycles (Figure 14). Visual examination of the membrane did not suggest any signs of degradation or swelling after this cycling test. This observation is consistent with the chemical stability of the Tokuyama membrane under acidic conditions. These results of repeated cycling confirm the viability of the new electrolyte composition and the use of the anion-exchange membrane separator for designing a high-efficiency iron-chloride flow battery.

Conclusions

We have demonstrated a high-efficiency iron-chloride redox flow battery with promising characteristics for large-scale energy storage applications. The advances demonstrated in this study show a path...
for the deployment of large-scale systems based on the iron-chloride flow battery concept originally discussed by Savinell and others. With a new electrolyte formulation consisting of complexing agents such as ascorbic acid, we were able to avoid precipitation of the iron hydroxides and stabilize the electrolyte at a pH value of 2. Further, with small amounts of indium chloride in the negative electrolyte, we were able to achieve charging efficiency values up to 97%. The high charging efficiency of the negative electrode was found to be stable over at least 50 cycles. High-surface area graphite felt electrodes reduced the overpotentials not only at the positive electrode but also the negative electrode. As a result, current densities $>$100 mA/cm² could be achieved even at room temperature. We have demonstrated that an iron-chloride flow battery design using an anion-exchange membrane separator with a unique formulation of the negative electrolyte provides significant advantages for long periods of operation, avoiding the difficulties of electrolyte crossover or precipitation. With the potential to achieve the objectives of high efficiency and low cost, the membrane-based iron-chloride flow battery could be a very attractive candidate for large-scale energy storage.

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