

The Effect of Electrolyte Composition on the Performance of a Single-Cell Iron–Chromium Flow Battery

Nico Mans, Henning M. Krieg,* and Derik J. van der Westhuizen

Flow batteries are promising for large-scale energy storage in intermittent renewable energy technologies. While the iron–chromium redox flow battery (ICRFB) is a low-cost flow battery, it has a lower storage capacity and a higher capacity decay rate than the all-vanadium RFB. Herein, the effect of electrolyte composition (active species and supporting electrolyte concentrations), Fe/Cr molar ratio, and supporting electrolyte type (HCl and H₂SO₄) on the performance (current efficiency (CE), voltage efficiency (VE), energy efficiency, discharge capacity, and capacity decay) of an ICRFB is investigated. The storage capacity of the optimum electrolyte (1.3 M FeCl₂, 1.4 M CrCl₃, 5.0 mM Bi₂O₃ in 1.0 M HCl) is 40% higher (from 17.5 to 24.4 Ah L^{−1}), while the capacity decay rate is tenfold lower (from 3.0 to 0.3% h^{−1}) than the performance of the previously used 1.0 M FeCl₂, 1.0 M CrCl₃ in 3.0 M HCl. At the optimum Fe and Cr concentrations and ratio in 0.5 M HCl, a near constant CE (92.3%), VE (78.7%), and EE (72.6%) are obtained over 50 cycles. The significantly higher capacity decay when using 1.0 M H₂SO₄ (1.6% h^{−1}) compared to 1.0 M HCl (0.3% h^{−1}) confirms that HCl is the more suitable supporting electrolyte.

electricity supplier, while simultaneously reducing the greenhouse gas emissions. Due to the intermittency of renewable energy sources such as solar, large scale electricity storage (LSES) systems are required. Due to various advantages, the redox flow battery (RFB) technology is regarded as one of the stationary LSES solutions.^[1–3]

The current front-runner in RFB technology, the all-vanadium flow battery (VRFB), outperforms the iron–chromium RFB (ICRFB) in terms of capacity, capacity retention, and efficiency due to the higher standard potential and superior electrochemical kinetics of, as well as less side reactions in, the electrolyte.^[2,4,5] The major concern associated with the VRFB remains the cost of storage (\$ kWh^{−1}), which results from the price of both the vanadium and the perfluorinated membranes required.^[1,2,6]

However, despite the VRFBs superior performance,

the ICRFB is one of the most cost-effective RFB technologies due to the abundance of both iron and chromium.^[2]

Numerous factors influence the performance of an RFB.^[7] For example, by developing new electrode materials and structures, both the energy and power density, and thus the overall performance of RFBs was improved.^[8,9] Similarly, electrolyte crossover and parasitic H₂ production contribute to self-discharge and capacity decay during ICRFB cycling, where the crossover is a function of the membrane, while the H₂ production is largely determined by the electrolyte.^[10,11] Current research is focusing on replacing the currently used Nafion membranes with cheaper alternatives, such as Speak, to reduce both the self-discharge and the cost of the VRFB and the ICRFB.^[12]

The electrolyte largely dictates the overall performance in an RFB,^[6] where the discharge capacity is determined by the concentration and volume of the active species and electrolyte while the energy density is determined by 1) the redox potential of the active species; 2) the number of cells within the stack; and 3) the electrode size.^[3] Both the active species (type, concentration, and ratio) and the supporting electrolyte (type and concentration) influence the overall RFB performance.^[13] Where the electroactive species stores or supplies energy during charge and discharge cycling by undergoing oxidation and reduction reactions,^[4,14] the supporting electrolyte influences the conductivity and the stability of the redox reactions.^[14,15] Where the active species concentration is directly proportional to the battery's storage capacity, the supporting electrolyte concentration is inversely proportional to the area-specific resistance (ASR) and thus the voltage efficiency.^[14,16]

1. Introduction

South Africa (SA), the world's largest ferrochrome producer, is currently experiencing an unstable electricity supply that is as yet still based on coal. This instability, stemming from significant technical and financial pressures faced by SA's national electricity provider, leads to frequent power outages that threaten the economy. The recent removal of the exemption threshold for private renewable energy generation (with or without storage), is facilitating the development of off-grid electricity, such as solar energy, taking advantage of SA's abundant sunshine. By addressing the country's electricity supply challenges, the renewable electricity generation will alleviate the strain on the national

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Since, both the active species and the supporting electrolyte influence the capacity decay rate of the battery, it is important to empirically determine the optimal electrolyte composition.

It was the aim of this study to investigate the effect of electrolyte composition on ICRFB performance by determining the influence of 1) the active species (Fe and Cr) concentrations; 2) the molar ratios (Fe/Cr); 3) the supporting electrolyte (HCl) concentrations; and 4) the supporting electrolyte type (HCl and H₂SO₄). These variables were investigated using a ICRFB cell that was operated for 10 cycles. After the optimizations, a 50-cycle run was done to validate the results obtained. From the results, it was evident that the overall performance of the ICRFB, especially in terms of capacity retention, could be improved significantly by finetuning the electrolyte composition.

2. Experimental Section

2.1. Cyclic Voltammetry

Cyclic voltammograms (CVs) were obtained using a three-electrode electrochemical cell (Metrohm) linked to a potentiostat/galvanostat (SP-240, Biologic, USA). For the three-electrode cell, a glassy carbon disc electrode (Metrohm) was used as the work electrode, platinum wire as the counter electrode, and an Ag/AgCl electrode (Metrohm) as the reference electrode. The CVs were measured in deoxygenated electrolytes at 25 °C and a scanning rate of 50 mV s⁻¹. CVs were used to evaluate the effect of bismuth on the redox behavior of the Fe²⁺/Fe³⁺ and Cr²⁺/Cr³⁺ half-reactions using a generic ICRFB electrolyte composition of 1.0 M FeCl₂·4H₂O (99.0%, Sigma-Aldrich), 1.0 M CrCl₃·6H₂O (98.0%, Sigma-Aldrich) in 3.0 M HCl (32%, Labchem), either with (5 mM) or without (0 mM) Bi₂O₃ (99.9%, Aldrich) in the electrolyte.^[2,17,18]

2.2. Flow Battery Setup and Operation

The testing setup (Figure 1) consisted of a lab-scale flow through RFB cell, two double-walled electrolyte reservoirs, and a dual-channel peristaltic pump (Watson-Marlow 323S). The operation of the ICRFB was controlled using a potentiostat/galvanostat (5000 E, Gamry), while a heating mantle in collaboration with a circulating water bath was used for temperature control. During operation, 45 mL of electrolyte was cycled through each half-cell at a flow rate of 50 mL min⁻¹.

An in-house manufactured (the NWU instrument makers) lab-scale flow-through single RFB cell (Figure 2) was used to measure the charge/discharge cycles. The cell (active area = 28 cm²) consisted of a proton exchange membrane (Nafion 212) sandwiched between two cell frames (Teflon), two carbon-felt electrodes with a specific thickness of 6.0 mm (GFA6 EA, SIGRACELL), two bipolar plates (TF6, SIGRACELL), and two copper current collectors, all held together by two aluminum endplates.

In all cases, 10 charge/discharge cycles were performed at a constant current density of 40 mA cm⁻² fluctuating between 1.25 and 0.75 V at (65 ± 2.5) °C (unless noted otherwise). From the charge/discharge curves measured, numerous performance indicators were calculated (Table 1). These include current efficiency (CE), voltage efficiency (VE), energy efficiency (EE), discharge capacity (Cap_{Dis}), discharge capacity decay (Cap_{Decay}),

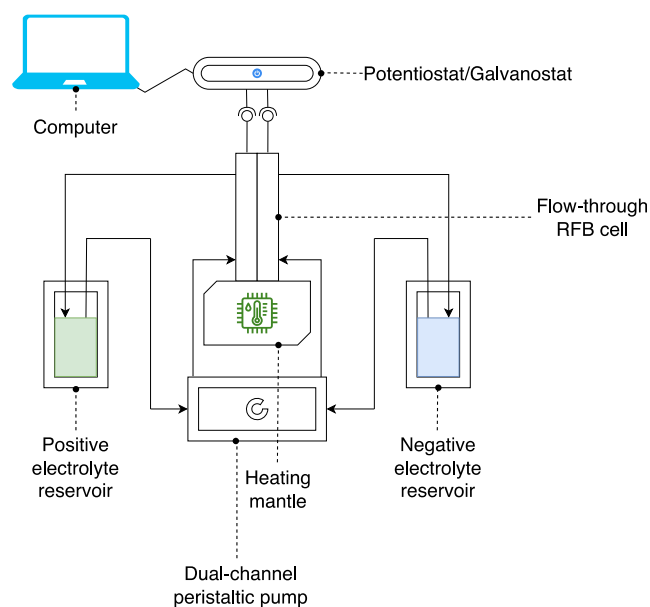


Figure 1. Schematic diagram of the ICRFB setup.

and capacity retention. The CE, VE, EE, and Cap_{Dis} values were reported for the first cycle (unless indicated differently), while the capacity decay and capacity retention were calculated over the 10 charge/discharge cycles.

2.3. Effect of Fe, Cr, and HCl Concentrations

To simultaneously assess the effect of the active species (Fe and Cr) and the supporting electrolyte (HCl) concentrations on the battery performance, an electrolyte range was prepared by dissolving 5.0 mM Bi₂O₃ (99.9%, Aldrich) and varying amounts of FeCl₂·4H₂O (99.0%, Sigma-Aldrich) and CrCl₃·6H₂O (98.0%, Sigma-Aldrich) with a Fe:Cr ratio of 1:1 in varying concentrations of HCl (32%, Labchem). The Bi₂O₃ was added as catalyst to all electrolytes tested to enhance the Cr²⁺/Cr³⁺ redox reaction.^[19] For each experiment, the electrolyte was freshly prepared and immediately used. The compositions of the various electrolyte combinations investigated are given in Table 2. Ten charge/discharge cycles were performed with each electrolyte using the procedure described in Section 2.2.

2.4. Effect of Fe/Cr Molar Ratio

To assess the effect of the active species (Fe/Cr) molar ratio on the battery performance, various electrolytes were prepared by dissolving 5 mM Bi₂O₃ (99.9%, Aldrich) and varying amounts of FeCl₂·4H₂O and CrCl₃·6H₂O in 1.0 M HCl to obtain the Fe/Cr molar ratios shown in Table 3. Ten charge/discharge cycles were performed with each electrolyte using the procedure described previously.

2.5. Effect of Supporting Electrolyte: HCl/H₂SO₄

To determine the effect of the supporting electrolyte, electrolytes were prepared in either HCl or H₂SO₄ by dissolving 5.0 mM

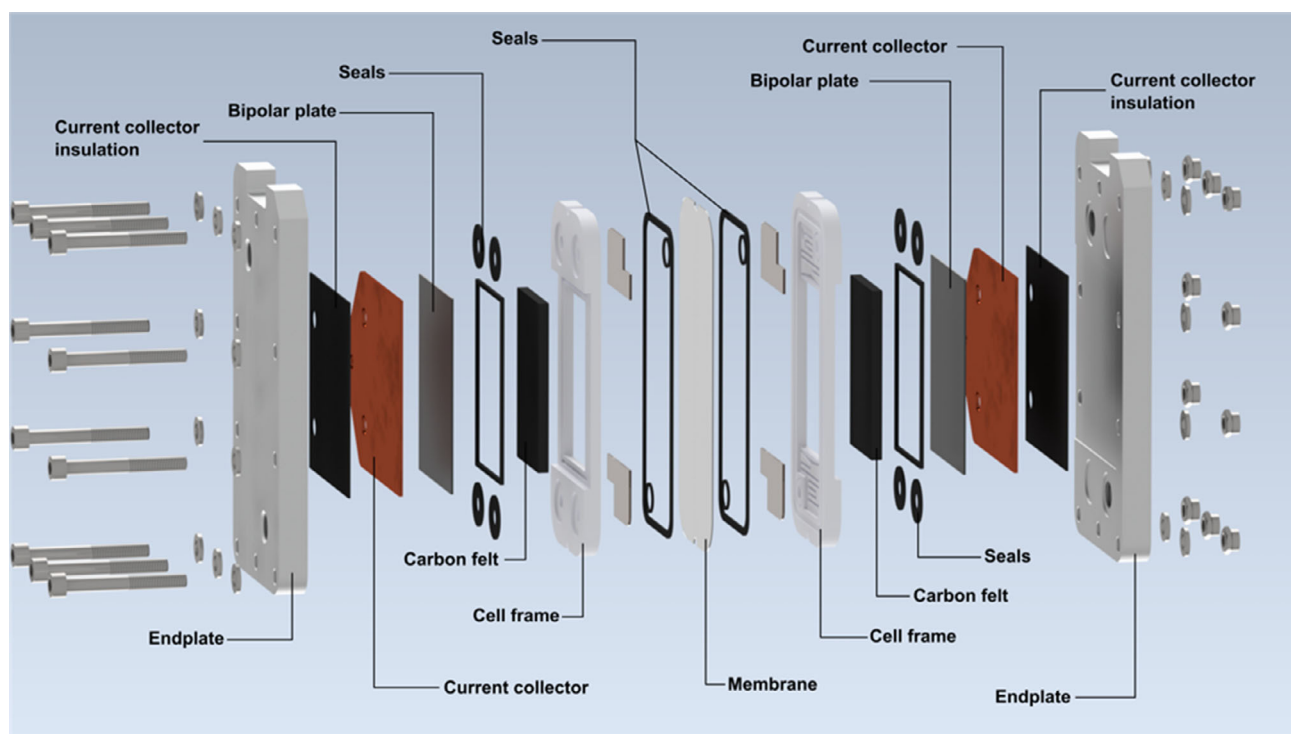


Figure 2. Schematic representation of the generic lab scale flow-through RFB cell used.

Table 1. Performance indicators used to evaluate ICRFB performance of various electrolytes tested.

Performance indicator	References
$CE (\%) = \frac{\text{Discharge capacity (Ah)}}{\text{Charge capacity (Ah)}} \times 100 \%$	[1,26]
$VE (\%) = \frac{\text{Average discharge voltage (V)}}{\text{Average charge voltage (V)}} \times 100 \%$	[1,26]
$EE (\%) = \frac{\text{Discharge energy (Wh)}}{\text{Charge energy (Wh)}} \times 100 \%$	[1,26]
$Cap_{Dis} (Ah L^{-1}) = \frac{\text{Discharge current (A)} \times \text{discharge duration (h)}}{\text{Electrolyte volume (L)}}$	
$Cap_{Decay} (\% h^{-1}) = \frac{\sum Cap_{Dis} (n-1)^{th} \text{ cycle (Ah)}}{Cap_{Dis} n^{th} \text{ cycle (Ah)}} \times 100\%$	
$Capacity \text{ retention } (\%) = \frac{Cap_{Dis} (n-1)^{th} \text{ cycle (Ah)}}{Cap_{Dis} n^{th} \text{ cycle (Ah)}} \times 100 \%$	[2]

Bi_2O_3 , 1.3 M $FeCl_2 \cdot 4H_2O$, and 1.4 M $CrCl_3 \cdot 6H_2O$ in varying concentrations of either HCl or H_2SO_4 (98%, Labchem), as shown in Table 4.

3. Results and Discussion

In Section 3.1, the effect of Bi_2O_3 on specifically the Cr redox reaction was investigated. This was followed by the results of the influence of varying Fe, Cr, and HCl concentrations (Section 3.2), the Fe/Cr ratio (Section 3.3), and finally iii) the type

Table 2. Electrolyte compositions (Fe/Cr molar ratio = 1:1) used to investigate the effect of active species and electrolyte concentration on ICRFB performance.

Electrolyte #	$FeCl_2 \cdot 4H_2O$ [M]	$CrCl_3 \cdot 6H_2O$ [M]	HCl [M]
1	1.0	1.0	1.0
2	1.1	1.1	1.0
3	1.2	1.2	1.0
4	1.3	1.3	1.0
5	1.4	1.4	1.0
6	1.5	1.5	1.0
7	1.0	1.0	2.0
8	1.1	1.1	2.0
9	1.2	1.2	2.0
10	1.3	1.3	2.0
11	1.4	1.4	2.0
12	1.5	1.5	2.0
13	1.0	1.0	3.0
14	1.1	1.1	3.0
15	1.2	1.2	3.0
16	1.3	1.3	3.0
17	1.4	1.4	3.0
18	1.5	1.5	3.0

of acid (Section 3.4). To further elucidate the influence of the HCl concentration and validate the optimization results based on only 10 cycles, the results of a 50-cycle run using an electrolyte

Table 3. Electrolyte compositions used to investigate the effect of the active species ratio on ICRFB performance.

Electrolyte #	FeCl ₂ ·4H ₂ O [M]	CrCl ₃ ·6H ₂ O [M]	Molar ratio (Fe/Cr)
19	1.3	1.1	1.18:1
20	1.3	1.2	1.08:1
21	1.3	1.3	1:1
22	1.3	1.4	0.93:1
23	1.3	1.5	0.87:1
24	1.1	1.3	0.84:1
25	1.2	1.3	0.92:1
26	1.3	1.3	1:1
27	1.4	1.3	1.08:1
28	1.5	1.3	1.15:1

Table 4. Electrolyte compositions used to investigate the effect of the supporting electrolyte on ICRFB performance.

Electrolyte #	HCl [M]	H ₂ SO ₄ [M]
29	–	1.0
30	–	2.0
31	–	3.0
32	1.0	–
33	2.0	–
34	3.0	–

comprising 1.3 M FeCl₂, 1.4 M CrCl₃, and 5.0 mM Bi₂O₃ in 0.5 M HCl are discussed in Section 3.5.

3.1. Effect of Bismuth

Cyclic voltammetry was used to assess the effect of bismuth on the redox behavior of the active species (Fe²⁺/Fe³⁺ and Cr²⁺/Cr³⁺) within the ICRFB electrolyte. To achieve this, CVs of two ICRFB electrolytes (1.0 M FeCl₂, 1.0 M CrCl₃ in 3.0 M HCl), one without (0 mM) and one with (5 mM) Bi₂O₃, were measured at 25 °C at a scan rate of 50 mV s^{−1}. The results are shown in Figure 3.

As shown in Figure 3, the addition of bismuth to the ICRFB electrolyte significantly enhanced the redox behavior of the Cr²⁺/Cr³⁺ redox couple, while also increasing the hydrogen overpotential, as confirmed by Xu et al. who showed the positive effect of Bi deposition on the performance of an ICRFB.^[19] Bismuth plates on the negative electrode during the start of the ICRFB charge cycle (Bi⁰-plating can be seen at ≈−0.4 V in Figure 3) where it facilitates the reduction of Cr³⁺ to Cr²⁺ and increases the hydrogen overpotential.^[20,21] It seems that the addition of Bi had a slightly negative influence on both the oxidation and reduction activity of the Fe²⁺/Fe³⁺ redox couple. While further electrochemical studies would be required to explain this occurrence, its effect was negligible compared to the significant improvement observed for the Cr²⁺/Cr³⁺ reaction kinetics. Based on these results, 5 mM Bi₂O₃ was added as a catalyst throughout this study.

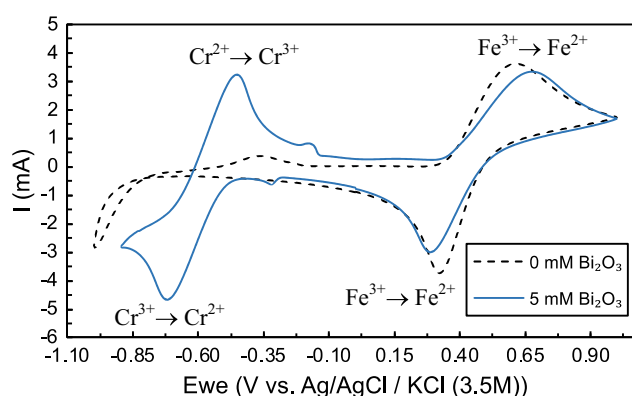


Figure 3. The effect of bismuth on the redox behavior of Fe²⁺/Fe³⁺ and Cr²⁺/Cr³⁺ in an electrolyte (1.0 M FeCl₂, 1.0 M CrCl₃ in 3.0 M HCl) measured at 25 °C.

3.2. Effect of Fe, Cr, and HCl Concentration

To assess the effect of both the active species (Fe and Cr) and the supporting electrolyte (HCl) concentrations on ICRFB performance, electrolytes containing 1.0–1.5 M Fe and Cr (Fe:Cr = 1:1) at three different HCl concentrations (1.0, 2.0, and 3.0 M) were evaluated. To calculate the various performance indicators, ten charge/discharge cycles were performed at 40 mA cm^{−2}, 65 °C, and between 1.25 and 0.75 V. The results of the first charge/discharge cycles are shown in Figure 4 for (a) 1.0 M, (b) 2.0 M, and (c) 3.0 M HCl by plotting the potential on the working electrode (*E*_{WE}) as a function of time. From the results, it is evident that the cycling time increased with increasing Fe and Cr (active species) concentrations independent from the HCl concentration reaching a maximum charge/discharge duration at 1.3 M active species. The increase in cycling time can be attributed to the fact that the theoretical capacity (expressed in Ah) of an RFB is given by Faradays law (Equation (1)), where the theoretical capacity (*Q*_{Theoretical}) is directly proportional to the active specie concentration (*c*), the volume of the electrolyte (*V*), and Faraday's constant (*F*).^[1,22] In addition to the increased cycling duration, a decrease in charge and increase in discharge voltage was also observed.

$$Q_{\text{Theoretical}}(\text{Ah}) = \frac{c \times V \times F}{3600} \quad (1)$$

3.2.1. CE, VE, and EE

The CE, VE, and EE as a function of varying Fe, Cr, and HCl concentrations are given in Figure 5a–c, respectively. It is known that the CE of a RFB is influenced by numerous factors including side reactions (such as H₂ generation), cross-over of active species, and osmosis of the electrolyte, over the membrane.^[1,23] One of the main causes of CE losses, specifically in the ICRFB, is due to H₂ production (hydrogen evolution reaction – Equation (2)), which is a parasitic side reaction on the negative electrode that irreversibly consumes charging current leading to a reduced CE.^[13–16]

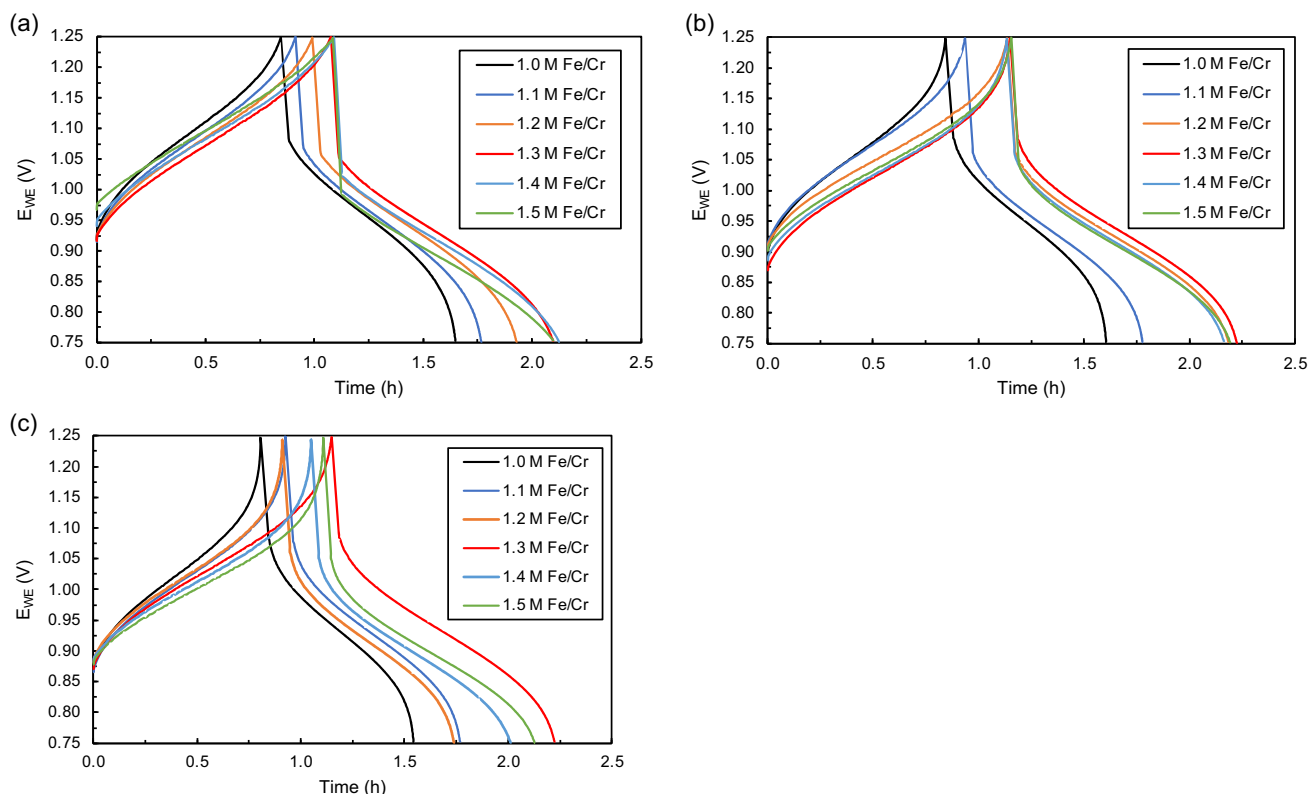


Figure 4. First charge/discharge curve as a function of the Fe and Cr concentration (1.0–1.5 M) at a Fe/Cr molar ratio of 1:1, as well as HCl concentration ($a = 1.0$ M, $b = 2.0$ M, and $c = 3.0$ M).



When studying the effect of the H_2SO_4 concentration on VRFB performance, Chen et al. obtained the following CE values with increasing H_2SO_4 concentration: 82.5% (0.5 M), 62.5% (1.0 M), 67.0% (2.0 M), and 70.0% (3.0 M), concluding that the CE decreased with increasing acid concentration.^[24] This would be expected considering the increased amount of H^+ ions with increasing HCl concentration, resulting in an increased H_2 production rate and hence a lower CE. This relationship was also observed in Figure 5a, where the highest CE values were obtained in 1.0 M HCl irrespective of the Fe and Cr concentrations. The difference in CE was less between 2.0 and 3.0 M HCl showing a slight increase in CE in 3.0 M HCl with increasing Fe and Cr concentrations. Chen et al. attributed the increase in CE at higher H_2SO_4 concentration to the increase in viscosity with increasing acid concentration.^[24] Similar increases in electrolyte viscosities have also been reported with increasing HCl concentrations.^[14,25] As the viscosity of the electrolyte increases with increasing acid concentration, the diffusion rate of H^+ ions decreases, resulting in a lower H_2 production and a higher CE.^[24]

From the curves shown in Figure 5a, it is also evident that the CE increased with increasing Fe and Cr concentration up to 1.3 M Fe and Cr independent of the HCl concentration before declining again. Wang et al. found that increasing the Fe and Cr concentration leads to a reduction in conductivity and an increase in viscosity.^[14] Consequently, the initial slight increase in CE with

increasing Fe and Cr concentration (up to 1.3 M), might be attributed to the increased viscosity, leading to a lower H^+ diffusion rate and, subsequently, a slightly higher CE.^[14,24] While the exact cause of the observed CE decrease at higher Fe and Cr concentrations (1.4 and 1.5 M Fe and Cr) is unknown, the highest CE value of 91.8% was obtained with 1.3 M of both Fe and Cr in 1.0 M HCl. In this study (Figure 5a), the conventional electrolyte composition for ICRFBs developed by NASA in the 1980s, consisting of 1.0 M of both FeCl_2 and CrCl_3 in 3.0 M HCl,^[2,14,18] delivered a CE value of 87.3%. This shows that a significant CE increase of 4.54% was obtained by increasing the active specie concentration to 1.3 M while decreasing the supporting electrolyte concentration to 1.0 M.

The VE as a function of the Fe and Cr (1.0–1.5 M) and HCl (1.0–3.0 M) concentrations, is presented in Figure 5b. It is known that the VE of a RFB is influenced by the ASR of the battery which, in turn, is primarily influenced by the conductivity of the membrane and secondary by the conductivity of the electrolyte.^[14] Since the same setup, operational conditions and membrane (Nafion 212) were used for all charge/discharge experiments, it can be assumed that the VE changes observed in this study resulted from changes in the electrolyte composition. According to Figure 5b, the VE increased with increasing HCl concentration while decreasing with increasing Fe and Cr concentrations. As the supporting electrolyte concentration (HCl) increases, the conductivity of the electrolyte increases, lowering the ASR of the battery.^[14,16] However, it has also been reported, that the conductivity of an

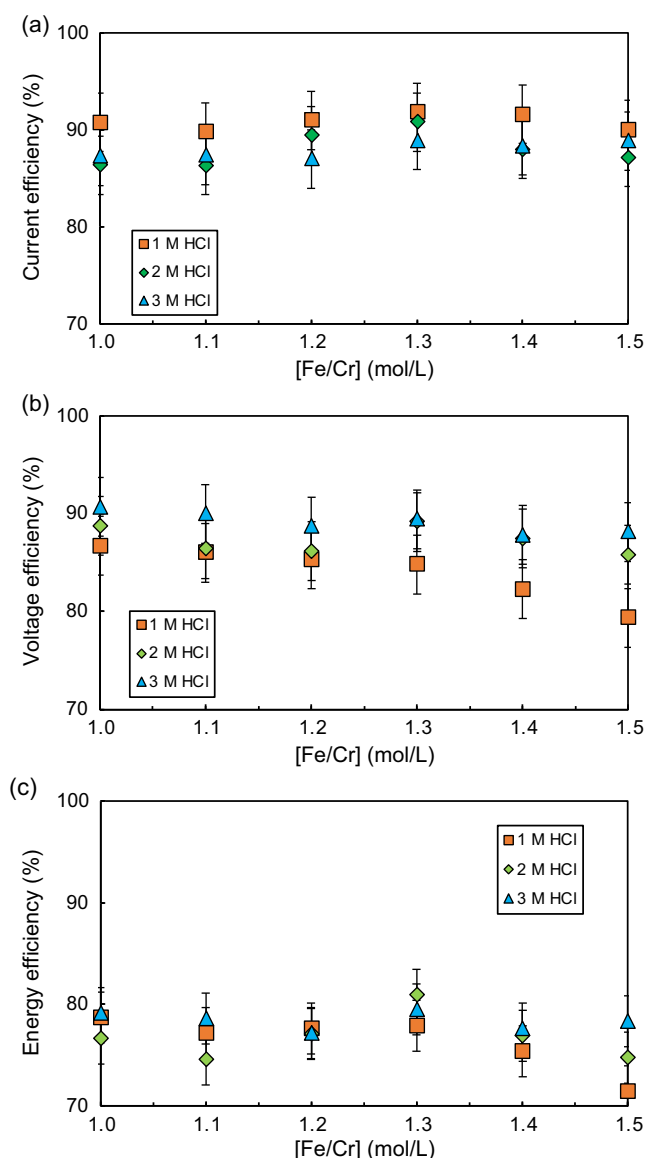


Figure 5. a) Current, b) voltage, and c) energy efficiencies (first charge/discharge cycle) as a function of the Fe and Cr (1.0–1.5 M), as well as the HCl concentration ($a = 1.0$ M; $b = 2.0$ M and $c = 3.0$ M) at a Fe/Cr molar ratio of 1:1 measured at 40 mA cm^{-2} and 65°C .

electrolyte decreases with an increasing active specie concentration, leading to an increasing ASR.^[14,16] From this study, it seems that the effect of the increasing Fe and Cr concentrations on the VE was more pronounced at 1.0 M HCl than at 2.0 and 3.0 M HCl, which could imply that the HCl, at higher concentrations, dominated the influence on the electrolyte conductivity. Due to the effect of conductivity on the ASR, the highest VE (90.7%) was obtained with an electrolyte with low Fe and Cr concentrations (1.0 M) and a high HCl concentration (3.0 M).^[14] Accordingly, the lowest VE (79.3%) was obtained at 1.5 M Fe and Cr and 1.0 M HCl, showing a significant VE increase of 11.3% when decreasing the active species concentration from 1.5 to 1.0 M while increasing the supporting electrolyte concentration from 1.0 to 3.0 M HCl.

The EE is a function of the Fe and Cr (1.0–1.5 M) and HCl (1.0–3.0 M) concentrations, as shown in Figure 5c. The EE of an RFB, which is the product and hence the combined effect of the CE and VE, gives an indication of how well energy conversion takes place in the battery.^[1] It is evident that the highest EE (80.9%) was obtained for an electrolyte consisting of 1.3 M Fe and Cr in 2.0 M HCl, which correlates well with the highest EE obtained for the NASA electrolyte (79.13%), confirming the importance of the electrolyte composition on the overall efficiency of an ICRFB.

3.2.2. Discharge Capacity and Capacity Decay

While the CE, VE, and EE provide important information on the efficacy of electrical conversion of the battery, it is equally important to determine the discharge capacity and capacity decay, which provide information on the amount of electricity that can be stored by the battery, as well as the capacity retained during battery operation.^[1] The discharge capacity and capacity decay of the electrolytes as a function of the Fe and Cr (1.0–1.5 M) and HCl (1.0–3.0 M) concentrations are given in Figure 6a,b, respectively. It is clear that the discharge capacity initially increased with increasing Fe and Cr concentration (up to 1.3 M Fe and Cr), independent of the HCl concentration, which is in line with the results obtained by Wang et al, who found that the discharge capacity increased from 10.71 to 21.43 Ah L^{-1} when increasing the Fe and Cr concentration from 0.5 to 1.0 M. According to Figure 6a, increasing the Fe and Cr concentration beyond 1.3 M (1.4 and 1.5 M Fe and Cr) seemed to have little effect on the discharge capacity, which is in line with the results obtained in Figure 5a. Since CE is an indication of how well charge electrons are regained during discharge, the decreasing CE values beyond 1.3 M Fe and Cr could be the cause for the observed plateau.

While the HCl concentration had a negligible effect on the discharge capacity (Figure 6a), its effect on capacity decay (Figure 6b) was significant showing an increased capacity decay with increasing HCl concentration. Since the same membrane was used for all tests, it can be assumed that the change in observed capacity decay might be attributed to side reactions such as parasitic H_2 production.^[26] The CE data (Figure 5a) had a similar tendency, which was ascribed to an increasing H_2 production with increasing HCl concentration. These results are also in line with those obtained by Wang et al. who found an increasing H_2 production rate with increasing supporting electrolyte concentration.^[14] When considering the influence of the active species concentration on the capacity decay, it seems that, initially, the decay decreased with increasing Fe and Cr concentrations, reaching a minimum at 1.3 M Fe and Cr before increasing again to 1.5 M. This again is similar to the trend observed for the CE values confirming the capacity decay is likely related to the H_2 production rate. Accordingly, the lowest capacity decay rate was obtained with an electrolyte consisting of 1.3 M Fe and Cr and 1.0 M HCl. The obtained capacity decay rate ($0.61\% \text{ h}^{-1}$) is 2.39% lower than that of the electrolyte consisting of 1.0 M Fe and Cr in 3.0 M HCl, which is a significant reduction in capacity decay leading to a reduction in the amount of rebalancing required during long-term RFB operation.

In this section, it was shown that by changing the Fe, Cr, and HCl concentrations from 1.0 M Fe and Cr in 3 M HCl to 1.3 M Fe

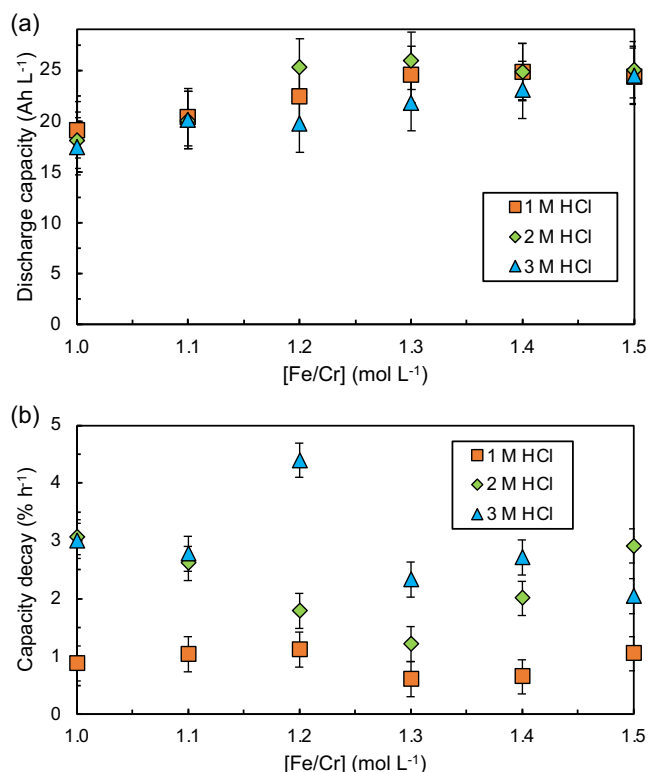
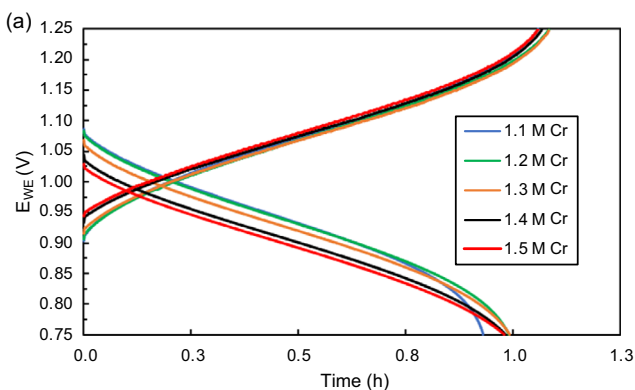


Figure 6. a) Discharge capacity and b) capacity decay as a function of the Fe and Cr (1.0–1.5 M), as well as the HCl concentration ($a = 1.0$ M, $b = 2.0$ M, and $c = 3.0$ M) at a Fe/Cr molar ratio of 1:1.

and Cr in 1.0 M HCl, the CE of the ICRFB was increased by 4.54%, while the VE was lowered by 5.84%. The observed increase in CE may be attributed to the decrease in amount of H⁺ ions available for hydrogen evolution, while the decrease in VE can be attributed to the reduced conductivity because of a lower supporting acid concentration. More importantly, considering the low-capacity and high-capacity decay of the ICRFB compared to that of the VRFB, the capacity decay rate was reduced by 2.39% while the discharge capacity was increased by 7.09%.



3.3. Effect of Fe/Cr Molar Ratio

The importance of the Fe, Cr, and HCl concentrations on the cycling performance of an ICRFB was clearly demonstrated in the previous section. In two patents (Chang et al.^[27] and Wei et al.^[28]), it is stated that the H₂ production reaction can be suppressed even further by increasing the Cr³⁺ concentration while keeping the Fe²⁺ concentration fixed.^[27,28] To verify this, the effect of the Fe²⁺/Cr³⁺ ratio on ICRFB performance was investigated using 1.0 M HCl as supporting electrolyte. Initially, the Cr³⁺ concentration was increased from 1.1 to 1.5 M at a constant Fe²⁺ concentration (1.3 M), before increasing the Fe²⁺ concentration from 1.1 to 1.5 M at a constant Cr³⁺ concentration (1.3 M).

The first charge–discharge cycles showing the effect of increasing Cr³⁺ and Fe²⁺ concentrations are shown in Figure 7a,b, respectively. It is evident that changing the initial Cr³⁺ concentration in the ICRFB (Figure 7a) had no significant effect on the charge/discharge capacity compared to that when varying the Fe²⁺ concentration (Figure 7b). This significant effect with varying Fe²⁺ concentration could be attributed to the fact that initially the Fe²⁺ is oxidized at the working electrode during charging, which subsequently leads (primarily) to the reduction of the Cr³⁺ ions and (secondary) to H₂-producing side reactions at the counter electrode. The slight increase in discharging duration with increasing Fe²⁺ concentration was expected considering that the Fe²⁺ concentration is the limiting factor during charging.

In Figure 8a,b, the effect of varying Cr³⁺ and Fe²⁺ concentrations on the CE, VE, and EE are shown. It seems that while increasing Cr³⁺ concentrations led to a slight increase in the CE, increasing Fe²⁺ concentrations led to a slight decrease in the CE. This increase in CE with increasing Cr³⁺ concentration can be attributed to the fact that when an RFB reaches higher state of charge (SOC) values, H₂ production increases due to increasing negative potentials at the negative (chromium) electrode.^[27] The SOC (Ω cm²) of the negative electrolyte (SOC_{Neg}; negative electrolyte state of charge (–)) can be expressed in terms of the Cr²⁺ ([Cr²⁺]) and the Cr²⁺ + Cr³⁺ ([Cr_{Total}]) concentrations in the solution. From Equation (3), it is evident that the SOC of the negative electrolyte will decrease when increasing the Cr³⁺ concentration in the electrolyte, leading to reduced negative voltages at the negative electrode thereby reducing the H₂ production rate and increasing CE values.

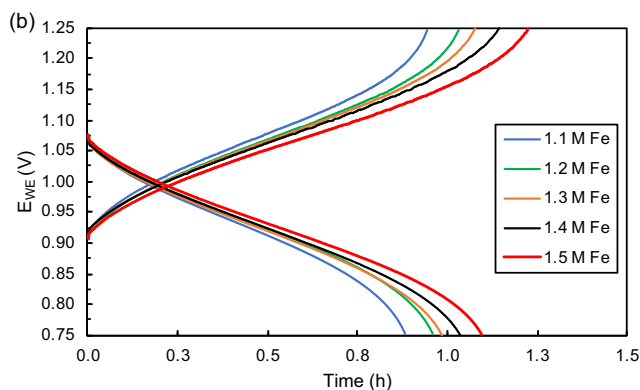


Figure 7. a) The effect of increasing Cr³⁺ concentration (1.1–1.5 M) at a constant Fe²⁺ concentration (1.3 M) and (b) increasing Fe²⁺ concentration (1.1–1.5 M) at a constant Cr³⁺ concentration (1.3 M) on the first charge/discharge cycle of the ICRFB.

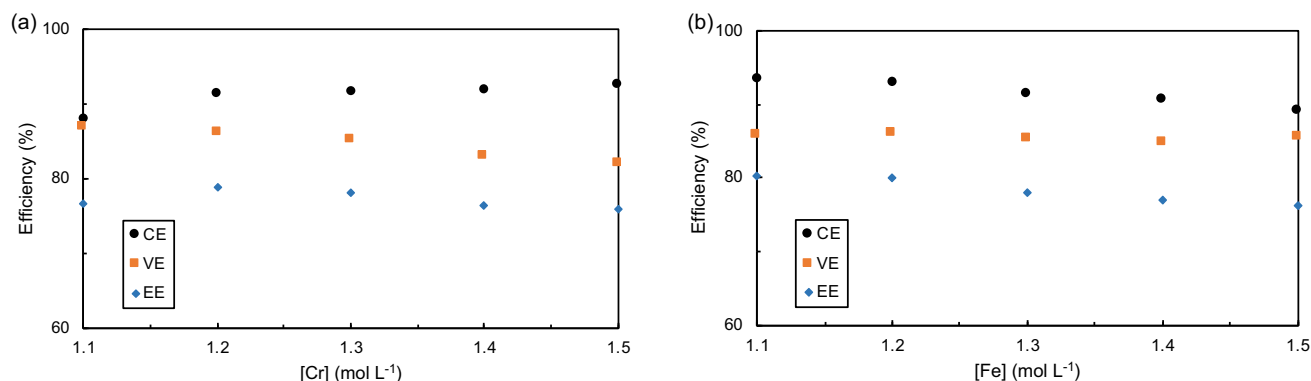


Figure 8. a) The effect of increasing Cr^{3+} concentration (1.1–1.5 M) at a constant Fe^{2+} concentration (1.3 M) and b) increasing Fe^{2+} concentration (1.1–1.5 M) at a constant Cr^{3+} concentration (1.3 M) on the CE, VE, and EE.

$$\text{SOC}_{\text{Neg}} = \frac{[\text{Cr}^{2+}]}{[\text{Cr}_{\text{Total}}]} \quad (3)$$

The observed decrease in CE with increasing Fe^{2+} concentrations (Figure 8b) might be attributed to the reactive electrochemical behavior of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple,^[2] i.e., during the charge cycle Fe^{2+} is easily oxidized with the resulting electrons flowing to the negative electrode via the external electrical circuit. At the negative (chromium) electrode, these electrons are not necessarily accepted by Cr^{3+} due to slower reaction kinetics and side reactions (such as H_2 production) that predominantly occur at the chromium side of the ICRFB resulting in lower CE values. Finally, in both cases (Figure 8a,b), a decrease in VE was observed with increasing Cr^{3+} or Fe^{2+} concentrations. Since the VE of an ICRFB is predominantly determined by the internal resistance of the battery, it is expected that the VE will decrease with decreasing electrolyte conductivity, which also corresponds to Wang et al. who observed a decreasing conductivity with increasing metal concentration in an ICRFB.^[14] Consequently, the reduced VE values observed in both cases were most likely due to a decreasing electrolyte conductivity due to the increasing Fe^{2+} or Cr^{3+} concentrations.

Finally, the effect of varying Cr^{3+} and Fe^{2+} ratios on the discharge capacity and capacity decay is presented in Figure 9a,b,

respectively. While the discharge capacity remained near constant with increasing Cr concentration (Figure 9a), it increased with increasing Fe concentration (Figure 9b). Again, this can be explained by the fact that the amount of Fe^{2+} oxidized at the working electrode determines the amount of Cr^{3+} reduced at the counter electrode. Hence, due to the decrease in SOC with increasing Cr^{3+} concentration, the capacity decay decreased with increasing Cr^{3+} concentration (Figure 9b). In the range 1.1–1.5 M Cr^{3+} (Figure 9a), a minimum capacity decay was reached at 1.4 M Cr^{3+} before increasing again.

The lowest capacity decay ($0.32\% \text{ h}^{-1}$) in combination with the highest discharge capacity (24.41 Ah L^{-1}) was obtained with an electrolyte consisting of 1.3 M FeCl_2 , 1.4 M CrCl_3 in 1.0 M HCl. Hence, by adding a small excess of CrCl_3 , the capacity decay was nearly halved from $0.61\% \text{ h}^{-1}$ (see Section 3.3.2) to $0.32\% \text{ h}^{-1}$ without significantly affecting the discharge capacity (24.60 vs 24.41 Ah L^{-1}).

3.4. Effect of Supporting Electrolyte: HCl/ H_2SO_4

Due to the known influence of the supporting electrolyte on the overall RFB performance, the influence of the type of supporting acid (HCl vs H_2SO_4) on the performance of the ICRFB was

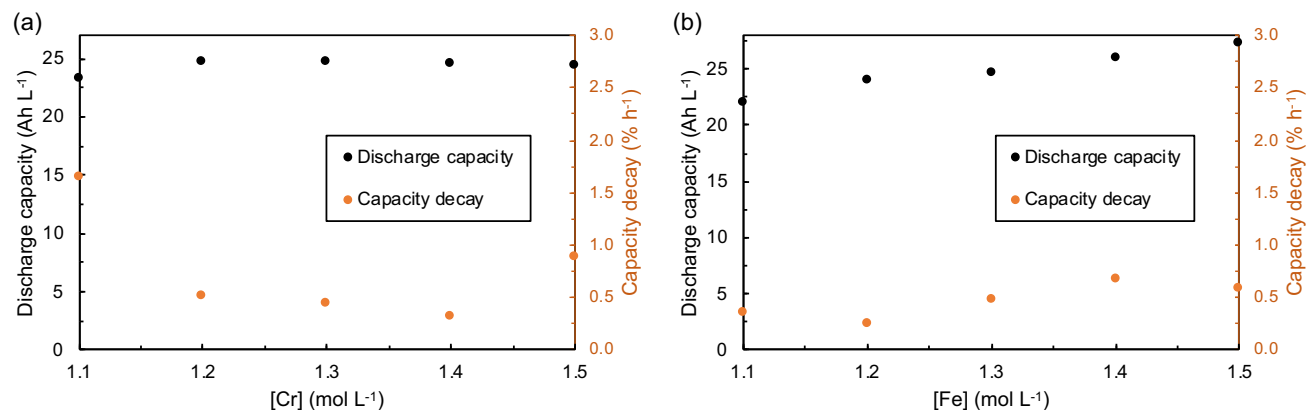


Figure 9. a) The effect of increasing Cr^{3+} concentration (1.1–1.5 M) at a constant Fe^{2+} concentration (1.3 M) and b) increasing Fe^{2+} concentration (1.1–1.5 M) at a constant Cr^{3+} concentration (1.3 M) on discharge capacity and capacity decay.

investigated. Only these two acids were investigated due the common use of H_2SO_4 in the VRFB and HCl in the ICRFB.^[29] In addition, HNO_3 is highly oxidizing and HF both poisonous and corrosive. While the effect of replacing HCl by H_2SO_4 on performance is unknown for the ICRFB, Li et al. clearly demonstrated the effect of supporting electrolyte on the VRFB performance. First, the storage capacity of the VRFB could be improved by as much as 70% when switching from the conventional H_2SO_4 supporting electrolyte to HCl , which they attributed to an increased vanadium solubility due to the decreased SO_4^{2-} ion concentration.^[29] Second, the operating temperature range of the VRFB could be improved from the original 10–40 to –5 to 50 °C, due to the formation of stable vanadium chloride aqueous species.^[29]

The effect of the supporting electrolyte type (HCl or H_2SO_4) on ICRFB performance was investigated at 65 °C and 40 mA cm^{–2} using 10 charge/discharge cycles. Both acids were tested at 0.5, 1.0, and 2.0 M. The effect of the H_2SO_4 and HCl concentration on the discharge capacity and capacity decay is shown in Figure 10a,b, respectively. As discussed previously (in accordance with Equation (1)), the supporting electrolyte did not have any significant influence on the discharge capacity which ranged between 23.1 and 25.1 Ah L^{–1} in H_2SO_4 and 24.4 and 26.5 Ah L^{–1} in HCl , respectively. However, the capacity decay per cycle increased significantly with increasing supporting electrolyte concentration for both H_2SO_4 (from 0.4 to 4.2% h^{–1}) and HCl (from 0 to 1.2% h^{–1}). It is also evident that the capacity decay increased significantly more with increasing H_2SO_4 concentration reaching over 4% h^{–1} at 2.0 M H_2SO_4 compared to the 1.2% h^{–1} obtained when using at 2.0 M HCl . This significant increase in H_2SO_4 , compared to that in HCl , likely results from H_2SO_4 being a diprotic acid as observed by Li et al. when studying this in a VRFB.^[29] The capacity decay of 0% h^{–1} at 0.5 M HCl (Figure 10b) confirms a negligible amount of irreversible side reactions (such as H_2 production) during cycling.

3.5. 50-Cycle ICRFB

Based on the previous results where 0.5 M HCl yielded the highest discharge capacity and lowest capacity decay, a 50-cycle feasibility study was done using 1.3 M FeCl_2 , 1.4 M CrCl_3 , 5.0 mM Bi_2O_3 in 0.5 M HCl . The efficiencies and discharge capacity as

a function of the number of cycles are shown in Figure 11a,b, respectively. During operation, a reduction in the positive electrolyte volume was observed. To assess whether the observed decrease in electrolyte volume (and consequently the observed decrease in discharge capacity) was due to electrolyte cross-over, the two electrolytes were remixed and repartitioned after 34 cycles (indicated on Figure 11) before completing another 16 cycles.

It is clear that the CE (92.3%), VE (78.7%), and EE (72.6%) remained near constant over 50 cycles in spite of the remixing and repartitioning (Figure 11a). According to Figure 11b, no significant capacity decay was observed (≈ 24.2 Ah L^{–1}) during the first 20 cycles confirming negligible H_2 production/side reactions. After 20 cycles, however, the capacity started to decrease reaching ≈ 20.0 Ah L^{–1} after 33 cycles. It was clear that the remixing and repartitioning did not restore the discharge capacity, which after a short rebound declined further reaching 18.31 Ah L^{–1} after 50 cycles. However, this decline did not affect the calculated efficiencies according to Figure 11a. Since it was evident from Figure 11b that the crossover was not responsible for the observed capacity decay starting after 20 cycles, the exact cause for the resulting positive electrolyte volume reduction (and observed capacity decay), when using 0.5 M HCl , is yet unknown and requires further investigation. One possibility might be the consumption of H_2O to compensate for the deficit of charge-carrying H^+ ions, which will have to be confirmed by adding water to the positive electrolyte and measuring the resulting effect on discharge capacity.

Since the observed capacity decay when using 0.5 M HCl requires further investigation, the optimal electrolyte composition was determined as 1.3 M FeCl_2 , 1.4 M CrCl_3 , and 5.0 mM Bi_2O_3 in 1.0 M HCl .

4. Conclusion

The aim of this study was to investigate the effect of ICRFB electrolyte constituents and concentrations on a single-cell performance. It was shown that by changing the conventional electrolyte composition (1.0 M FeCl_2 , 1.0 M CrCl_3 in 3.0 M HCl) to 1.3 M FeCl_2 , 1.4 M CrCl_3 in 1.0 M HCl , the CE increased by 5%, while the VE and EE reduced by 8% and 4%, respectively. In addition, it also led to an increased storage capacity (from 17.51 to 24.41 Ah L^{–1}) and, even more importantly, a reduction in the

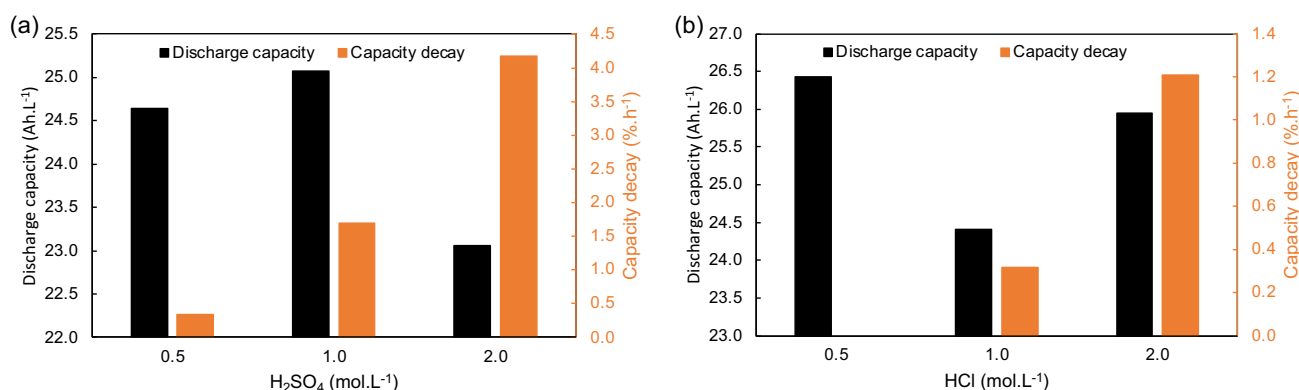


Figure 10. The effect of a) H_2SO_4 and b) HCl concentration on discharge capacity and capacity decay.

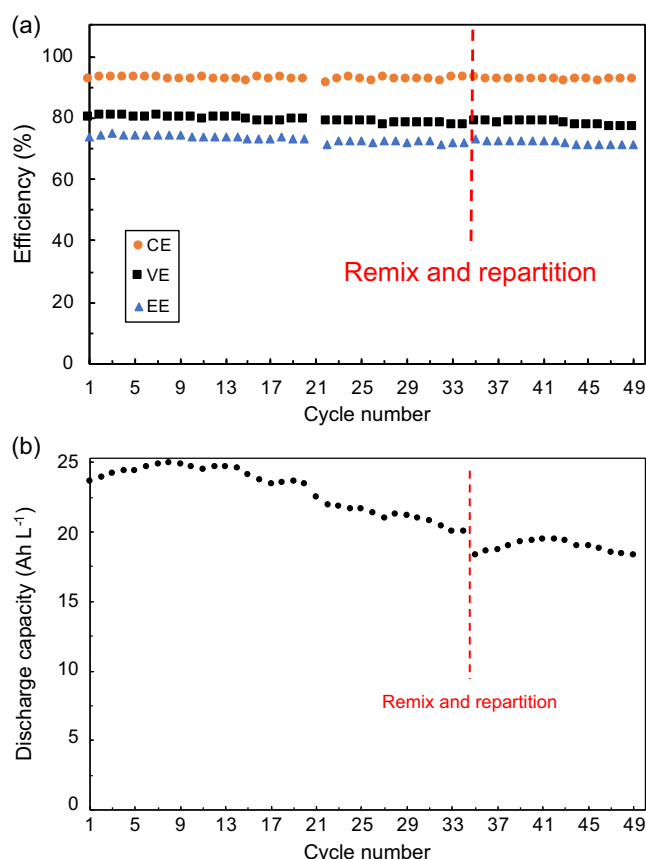


Figure 11. a) CE, VE, and EE as well as b) capacity retention of a 1.3 M FeCl₂, 1.4 M CrCl₃, and 0.5 M HCl electrolyte over 50 cycles.

capacity decay by a factor of ten (from 3.0 to 0.3% h⁻¹), which is comparable to that of the VRFB. Finally, a capacity decay of 0.0% was achieved (over the first 20 charge/discharge cycles) by reducing the HCl concentration further to 0.5 M. This composition did, however, lead to significant positive electrolyte volume reduction after 34 cycles, which will require further development to determine the feasibility of long-term operation using 0.5 M HCl.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

capacity decay, efficiency, electrolyte compositions, iron–chromium redox flow batteries, single cell performance, storage capacity

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