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# The Effect of Bismuth on the Performance of a Single-Cell Iron–Chromium Redox Flow Battery

*Nico Mans, Derik van der Westhuizen, and Henning Manfred Krieg**

**This study examines the need for bismuth as a catalyst for the $Cr^{2+}/Cr^{3+}$ redox couple in an iron–chrome redox flow battery (ICRFB) using 1) open-circuit voltage (OCV) periods to understand the impact of bismuth and the mechanism of hydrogen production with and without electrolyte flow, and 2) charge/discharge cycles to evaluate how bismuth influences ICRFB performance. The OCV study finds that the capacity decay in the ICRFB cycling is not solely due to the hydrogen evolution reaction, suggesting an alternative oxidation reaction is involved, likely catalyzed by metallic carbides like bismuth carbide. Both the OCV and the ICRFB confirm that the presence of bismuth negatively influences the battery performance due to increased $H_2$ production. Further research is ongoing to validate the decay mechanism and confirm these results on a larger scale.**

## 1. Introduction

One of the main advantages of redox flow batteries (RFBs) for large-scale and long-discharge duration energy storage is the flexibility gained by the decoupling of power (battery stack) and storage (electrolyte tanks).[1] Although the all vanadium RFB (VRFB) is currently the most widely used RFB, the iron–chrome RFB (ICRFB) is receiving renewed interest due to, among other, its significantly lower cost and less oxidative environment.[2] One of the important components in any RFB, such as the ICRFB, is the carbon felt electrode providing the active surface where the electrochemical oxidation and reduction reactions occur.[3] The electrode should offer a high electrochemical activity for the applicable redox reactions. The positive electrode couple ($Fe^{2+}/Fe^{3+}$) in an ICRFB generally shows repeatable and excellent kinetic performance on the carbon-based electrodes.[4] During NASA's Redox Storage System Development project in the 1980s, it was, however, shown that the negative electrode couple ($Cr^{2+}/Cr^{3+}$) has sluggish reaction kinetics.[5] This has led to significant developments to improve these kinetics by varying operating condition, electrolyte compositions, membrane, catalysts, and electrodes.[4,6,7] Various articles have reported improved performances by modifying the electrodes, including Zhang et al. who used thermally activated polyacrylonitrile-based graphite felts,[8] Chen et al. who used Bi-deposited thermally treated graphite felts,[9] and Ahn et al. who used Ketjenblack carbon with embedded bismuth nanoparticles.[10] The addition of catalysts has been shown to enhance the electrochemical activity, while increasing the overpotential for $H_2$ reduction ultimately suppressing the hydrogen evolution reaction (HER: $2H^+ + 2e^- \rightarrow H_2$ ($E = 0$ V vs SHE)), during battery cycling.[6]

During large-scale tests, NASA also found that the negative (Cr) electrolyte showcased a low charge acceptance rate, reaching only 50% state of charge (SOC), while the volumes for lab-scale tests were small enough for this phenomenon to be negligible.[5,11] The low charge acceptance rate was attributed to aqueous speciation of the chromium species where two $Cr^{3+}$ complexes were identified within the electrolyte, an electrochemically active species ($Cr(H_2O)_5Cl^{2+}$), and an electrochemically inactive species ($Cr(H_2O)_6^{3+}$). It is well known that aqueous speciation depends on solution conditions such as temperature and acidity.[12] Gahn et al. showed that increasing the temperature to 65 °C shifted the equilibrium toward the electrochemically active species, which allowed the electrolyte to be charged up to 90% SOC.[11] These results have confirmed the importance of aqueous speciation on the performance of an ICRFB during cycling.

While the addition of the Bi catalyst was initially proposed to improve the sluggish reaction kinetics, the requirement for a catalyst such as Bi should be reviewed: 1) It was shown that an electrolyte composition of 1.3 M $FeCl_2$, 1.4 M $CrCl_3$, and 5 mM $Bi_2O_3$ performed better (in terms of capacity and capacity retention) than the electrolyte composition initially proposed by NASA (1.0 M Fe, 1.0 M Cr, and 10 mM Bi in 3 M HCl)[13]; 2) The initial research by NASA on identifying a suitable catalyst (Bi) was done at 25 °C; 3) The shift to higher temperatures (65 °C) results in a shift toward an electrochemically more active species within the electrolyte[11]; 4) The alteration in electrolyte composition of the newly developed electrolyte will most likely lead to changes in speciation; and 5) Bismuth (which plates during the first charging cycle) will deplate during deep discharge of the battery introducing the need for a bismuth-management system in ICRFBs.

In this study, the effect of bismuth on the charge/discharge performance of an ICRFB was investigated using both open-circuit voltage (OCV) and charge/discharge cycles. Finally,

N. Mans, D. van der Westhuizen, H. M. Krieg
RFA for Chemical Resource Beneficiation
North-West University
11 Hoffman Street, Potchefstroom 2530, South Africa
E-mail: henning.krieg@nwu.ac.za

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/aesr.202400113.



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Faraday's equation was used to determine the influence of bismuth on the amount of $H_2$ produced.

## 2. Results and Discussions

### 2.1. Effect of Bi During the OCV Period

As discussed, the use of bismuth as a catalyst for the $Cr^{2+}/Cr^{3+}$ redox couple was proposed in the 1980s. While various alternative catalysts, such as indium[14,15] or $SiO_2$[16] based systems, have been developed and tested showing promising results, bismuth is still often used. However when considering that the composition of the electrolyte has changed significantly in recent years[13] from the one developed by NASA, the question whether Bi is actually required is worth pursuing. To assess the effect of bismuth not only during operation but in the absence of electron flow as well, various electrolytes were subjected to an identical charge procedure after which they were either 1) discharged immediately; 2) discharged after a 1 h OCV period during which the electrolyte was not circulated; or 3) discharged after a 1 h OCV period during which the electrolyte was circulated. The resulting charge/discharge curves are shown in the presence (5 mM $Bi_2O_3$) and absence of bismuth in **Figure 1**a,b, respectively. Note that the discharge curve of both experiments, where an 1 h OCV period was included, was shifted to the right by 1 h showing the real-time effect of the OCV period. Faraday's law was subsequently applied to the obtained discharge curves to gain insight into possible parasitic $H_2$ side reactions.

The influence of the OCV period on the discharge capacity in the presence and absence of Bi is shown in **Figure 2**. Initially, as expected, the presence of Bi did improve the kinetics yielding a higher discharge capacity. However, when introducing an OCV period, the Bi contributed to a faster decrease in the discharge capacity, which was exacerbated when circulating the electrolyte past the Bi containing electrode.

During the OCV period both without and with circulation, the discharge capacity decreased more in the presence of Bi than when no Bi was present. Two phenomena could be responsible for the observed decrease: 1) parasitic side reactions and/or 2) self-discharge. In 2020, Cho et al. showed that it took ≈5 h for self-discharge to have a noticeable effect on the SOC of a VRFB when using Nafion 212,[17] which would hence make it unlikely for self-discharge to have such a significant effect in the 1 h OCV period used in this study. Consequently, it can be assumed that the observed $Cap_{Dis}$ decrease was primarily caused by parasitic hydrogen production. Significant gas formation within the cell was observed during experimental runs at the negative side of the battery during OCV periods where the bismuth catalyst had been added, further supporting the theory that the capacity loss was mainly caused by parasitic $H_2$ production.

Using Faraday's equation (Equation (3)), the decrease in the moles of $Cr^{2+}$ present at the start of the discharge cycle after the OCV periods for the respective discharge capacity decreases was calculated (**Table 1**). As the decrease of the $[Cr^{2+}]$ was most likely caused by an increase in $H_2$ production, the change in $Cr^{2+}$ due to the OCV period was used to calculate the amount of $H_2$ produced. As no electron flow occurs between the positive and negative electrode during OCV periods, it is improbable that the HER (requiring electron flow) is solely responsible for the observed capacity reduction. Therefore, it is likely that another reaction was responsible for the $H_2$ production during the OCV period. Considering the theoretical electrolyte composition of a fully charged negative ICRFB electrolyte (1.3 M $FeCl_2$, 1.3 M $CrCl_2$ in 2 M HCl, where $Cr^{2+}$ is the electrochemically active species), the most likely decay mechanism is proposed in Equation (1) where the $Cr^{2+}$ in the presence of HCl is oxidized to $Cr^{3+}$ and $H^+$ is reduced to $H_2$, with a calculated

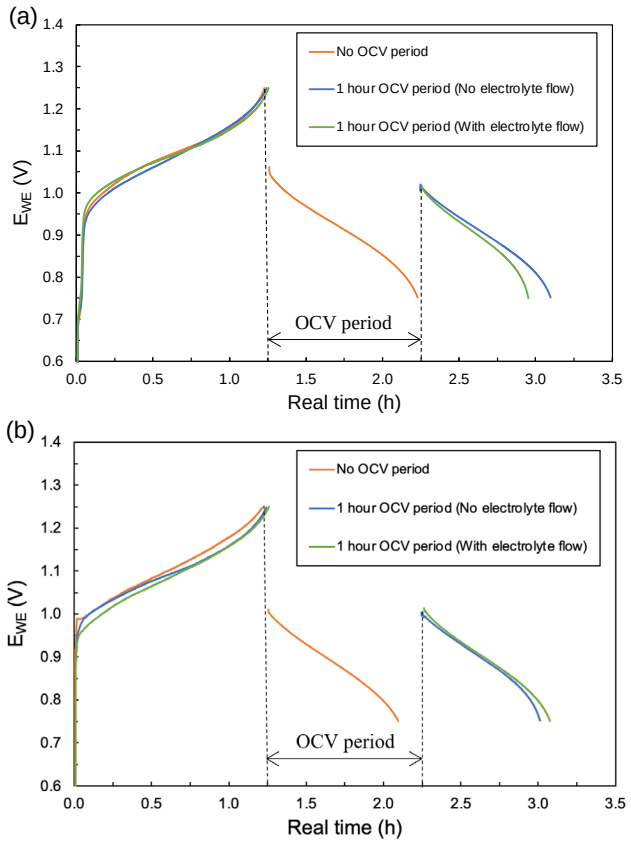


**Figure 1.** The effect of an OCV period on discharge capacity for an electrolyte containing a) 5 mM $Bi_2O_3$ or b) 0 mM $Bi_2O_3$.

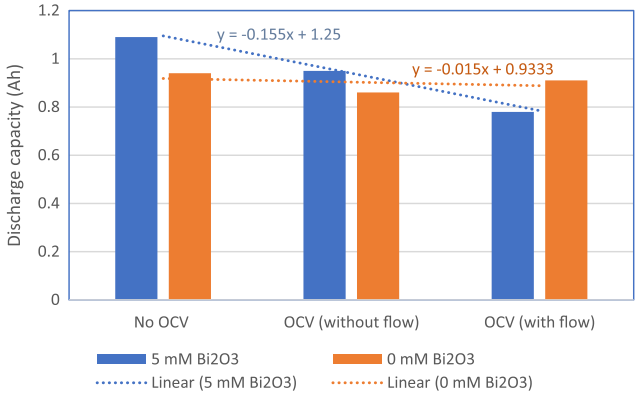


**Figure 2.** Influence of the presence of Bi on the discharge capacity without and with an OCV period (with and without circulation).

**Table 1.** The effect of various OCV periods on the discharge capacity and $H_2$ production in the presence or absence of bismuth as a catalyst.

| | $Cap_{Dis}$ [Ah] | Decrease in $Cap_{Dis}$ [Ah] | Decrease in $[Cr^{2+}]$ [$\times 10^{-3}$ mol] | Increase in $H_2$ production [mL] |
|---|---|---|---|---|
| 5 mM $Bi_2O_3$ | | | | |
| No OCV | 1.09 | – | – | – |
| 1 h OCV (without flow) | 0.95 | 0.14 | 5.00 | 56.03 |
| 1 h OCV (with flow) | 0.78 | 0.31 | 11.46 | 128.32 |
| 0 mM $Bi_2O_3$ | | | | |
| No OCV | 0.94 | – | – | – |
| 1 h OCV (without flow) | 0.86 | 0.08 | 2.24 | 25.07 |
| 1 h OCV (with flow) | 0.91 | 0.03 | 1.12 | 12.54 |

$\Delta G = -34.81\ \mathrm{kJ\ mol^{-1}}$, confirming that this reaction can occur spontaneously.

$$2CrCl_{2(Aq)} + 2HCl \rightarrow 2CrCl_3 + H_2 \quad (1)$$

In addition, when comparing the capacity of the discharge cycle where the OCV period occurred without and with electrolyte flow, it is evident that the capacity loss increased in the presence of electrolyte flow. This increased capacity loss was likely related to the fact that during flow, all of the charged electrolyte could come into direct contact with the negative electrode on which the bismuth had been plated. This observation could be an indication that the reaction shown in Equation (1) is catalyzed by the plated bismuth carbide. This seems to indicate that the bismuth that is known to facilitate the $Cr^{3+}$ reduction reaction also catalyzes other side reactions.

When considering the results presented by Mans,[18] where it was shown that metals that plate on the negative electrode generally result in higher $H_2$ production rates during cycling, it can be assumed that the side reaction (Equation (1)) is not necessarily only catalyzed by bismuth carbide but could also be catalyzed by other metal impurities (such as NiC) leading to Equation (2) (where MeC is a metal carbide).

$$2CrCl_{2(Aq)} + 2HCl \xrightarrow{MeC} 2CrCl_3 + H_2 \quad (2)$$

This theory seems to be supported by the results where bismuth was not added to the electrolyte (see Figure 1 and). It is evident that the absence of bismuth resulted in a $[Cr^{2+}]$ reduction that was less than half after 1 h OCV without flow and approximately a tenth after 1 h OCV without flow compared to when bismuth was present. In addition, the flow of the electrolyte in the absence of bismuth during the OCV period seemingly had no significant effect with the slight discrepancy between the two cases most probably due to small electrolyte composition differences. Further confirmation was the fact that no significant gas formation was observed on the negative side of the RFB during the experiments where no bismuth had been added. Although proving the alternative decay mechanism suggested herein (Equation (1)) was beyond the scope of this study, it would explain various RFB behaviors observed during cycling, such as $H_2$ production during discharge that should be investigated further.[19]

### 2.2. Effect of Bi During ICRFB Cycling

According to the results from the previous section, it is evident that substantially fewer $H_2$-producing side reactions occurred during OCV periods in the absence of Bi when using the newly developed electrolyte composition. As Bi was initially added to enhance the electrochemical activity of the $Cr^{2+}/Cr^{3+}$ redox couple and suppress the HER, it is essential to verify the effect of bismuth on the ICRFB charge/discharge behavior. To assess the effect of bismuth on the charge/discharge performance of the ICRFB, an electrolyte with (5 mM) and without $Bi_2O_3$ was subjected to ten charge/discharge cycles. The calculated coloumbic, voltage and energy efficiencies (CE, VE, EE), and capacity discharge for ten cycles in the presence and absence of Bi are shown in **Figure 3**a,b, respectively.

It is evident from Figure 3 that the exclusion of bismuth led to a significant increase in CE (from 90% to 93%), which is in line with the results shown in Table 1. Naturally, the observed increase in CE also led to an increase in both EE (from 74% to 76%) and discharge capacity (from 24.22 to 25.66 Ah $L^{-1}$). In contrast, the VE was virtually unaffected by the presence of bismuth.

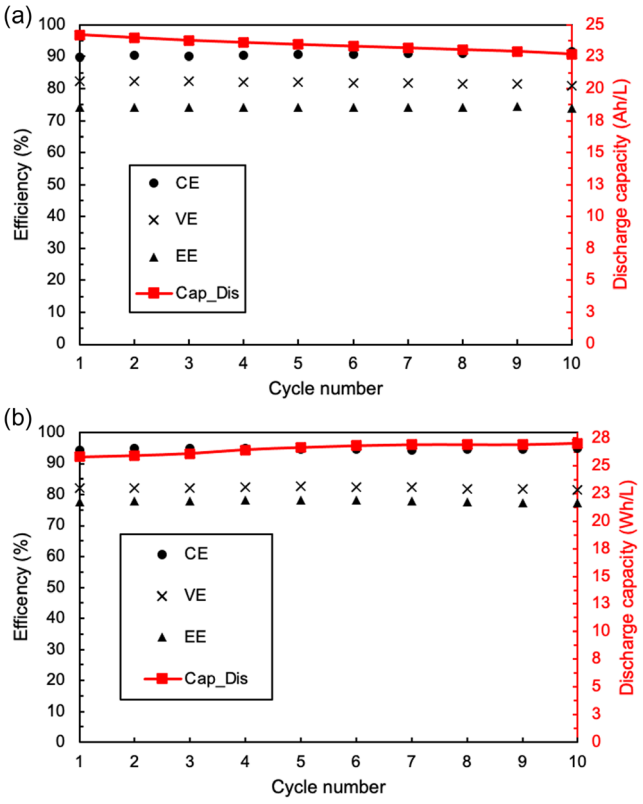


**Figure 3.** CE, VE, EE, and discharge capacity over ten cycles for an electrolyte containing a) 5 mM $Bi_2O_3$ and b) 0 mM $Bi_2O_3$.

In fact, it seems that the omission of bismuth led to a slight increase in the discharge capacity over the first ten cycles (from 25.66 to 27.12 Ah $L^{-1}$). This unexpected phenomenon most likely resulted from the crossover of metal species during the first few cycles.[20] Due to the applied current, $Fe^{2+}$ ions initially migrate from the negative (Cr) electrolyte to the positive electrolyte, while $Cr^{3+}$ ions migrate from the positive (Fe) electrolyte to the negative electrolyte. The migration leads to an increase in active species concentration in the respective electrolyte reservoirs, resulting in the observed capacity increase until equilibrium is reached. It should be noted that this migration behavior most probably has nothing to do with the presence/absence of bismuth but rather that this increase in capacity (when using bismuth a as catalyst) is dominated by the larger decay rate as a result of higher $H_2$ production rates.

By comparing Figure 3a,b, it is evident that the omission of bismuth significantly increased the CE while reducing the capacity decay per cycle. Consequently, by omitting bismuth as a catalyst from the ICRFB electrolyte, it would be expected that significantly less rebalancing would be required during long-term real-world applications.[21] In addition, due to the migration of active species, there exists an apparent increase in discharge capacity, as discussed in the previous paragraph. To assess the feasibility of long-term cycling when omitting bismuth and to simultaneously obtain an accurate decay rate over more cycles, an electrolyte consisting of 1.3 M $FeCl_2$, 1.4 M $CrCl_3$ in 1.0 M HCl was subjected to long-term cycling (100 cycles) of which the results are shown in **Figure 4**a,b.

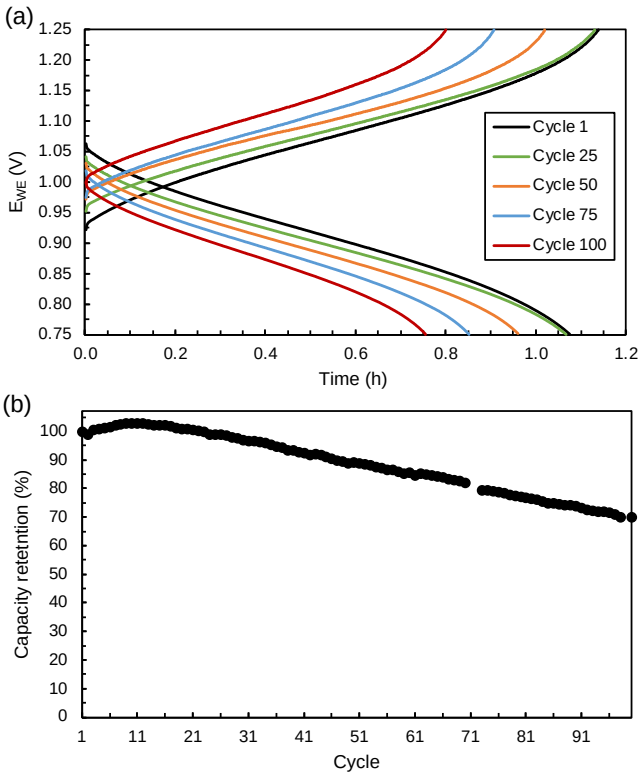


**Figure 4.** Long-term cycling results—a) charge/discharge curves and b) capacity retention—for an ICRFB electrolyte consisting of 1.3 M $FeCl_2$, 1.4 M $CrCl_3$ in 1.0 M HCl measured at 40 mA $cm^{-2}$ and 65 °C.

From Figure 4b it is evident that after 100 cycles (>194 h), the ICRFB retained 70.14% of its original discharge capacity. The retention of 70.14% of the ICRFBs discharge capacity over 100 cycles equates to a capacity decay rate of only 0.15% $h^{-1}$. Considering the 0.33% $h^{-1}$ decay observed in the presence of bismuth over the first ten cycles, it is clear that the omission of bismuth as a catalyst is not only feasible but also improves the overall cycling performance of the ICRFB.

## 3. Conclusion

In this study, the requirement for bismuth as a catalyst in an ICRFB for the $Cr^{2+}/Cr^{3+}$ redox couple was investigated using both OCV and cycling. According to the OCV results, the HER is not solely responsible for the capacity decay experienced during ICRFB cycling, indicating that an alternative oxidation reaction was, at the least, partially responsible for the observed decay. In addition, it would appear that the aforementioned oxidation reaction was catalyzed via metallic carbides such as bismuth carbide. Charge/discharge cycles were subsequently used to empirically investigate the effect of the omission of bismuth as a catalyst on the charge/discharge behavior of the ICRFB when using the newly developed electrolyte. Surprisingly, the omission of bismuth was found not only to be feasible for long-term cycling but also lead to improved cycling performance. Future work should confirm the proposed decay mechanism, as well as the confirmation of these results on a larger scale.

## 4. Experimental Section

*Materials and RFB Test Setup*: Electrolytes were prepared using 1.3 M $FeCl_2.4H_2O$ (99.0%, Sigma–Aldrich), 1.4 M $CrCl_3.6H_2O$ (98.0%, Sigma–Aldrich), and 0 or 5 mM $Bi_2O_3$ (99.9%, Aldrich) in 1.0 M HCl (32%, Labchem), which were all used without any additional purification. A potentiostat/galvanonstat (Gamry 5000E) and a generic lab-scale RFB (NWU instrument makers)[13] were used to measure charge/discharge cycles. The generic lab-scale flow-through single RFB cell had an active area of 28 $cm^2$. The cell consisted of a proton exchange membrane (Nafion 212) sandwiched between two cell frames (Teflon), two carbon felt electrodes (GFA6 EA, SIGRACELL), two bipolar plates (TF6, SIGRACELL), and two copper current collectors; all held together by two aluminum endplates. Charge/discharge cycles were performed at a constant current density of 40 mA $cm^{-2}$ between 1.25 and 0.75 V at (65 ± 2.5) °C. A volume of 45 mL of electrolyte was cycled through each half-cell at a flow rate of 50 mL $min^{-1}$ using a dual-channel peristaltic pump (Watson-Marlow 323S).

*Effect of Bi During the OCV Period*: To measure the effect of Bi's in the absence of electron flow between the positive and negative electrodes, an OCV period was used. Two electrolytes, either containing 0 or 5 mM $Bi_2O_3$, were charged to 1.25 V. After the charge cycle was completed, the electrolytes were subjected either to 1) no OCV period; 2) a 1 h OCV period without electrolyte flow; or 3) a 1 h OCV period with electrolyte flow. Following the OCV periods, the respective electrolytes were discharged to 0.75 V to be able to compare the resulting discharge curves with and without an OCV period.

According to Faraday's equation (Equation (3)), the discharge capacity is directly proportional to the amount of $Cr^{2+}$ present within the electrolyte before discharging.

$$Q = \frac{n \times F}{3600} \quad (3)$$

where $Q$ refers to the discharge capacity (Ah), $n$ refers to the moles of $Cr^{2+}$, and $F$ is the Faraday's constant (96 485 C $mol^{-1}$). It is well known that hydrogen production (irrespective of the mechanism) reduces the amount of $Cr^{2+}$ within the electrolyte. Consequently, as the two respective electrolytes were charged under identical conditions in the same RFB cell, any differences in the discharge capacity could be ascribed either to the effect of Bi, or the conditions (with or without circulation) under which the OCV period was performed. Accordingly, using the measured discharge capacities, the amount of moles of $Cr^{2+}$ present in the electrolyte prior to discharge was calculated using Faraday's equation. Considering that hydrogen production reduces the $Cr^{2+}$ content, the differences between the $Cr^{2+}$ content of the charged electrolytes were used to calculate the relative amount of $H_2$ produced during either the charge cycle or the OCV period.

*Effect of Bi During Charge/Discharge Cycles*: The setup described in Section "Materials and RFB Test Setup" was used to measure the charge/discharge cycles. Electrolytes consisting of 1.3 M $FeCl_2.4H_2O$ (99.0%, Sigma–Aldrich), 1.4 M $CrCl_3.6H_2O$ (98.0%, Sigma–Aldrich), and 0 or 5 mM $Bi_2O_3$ (99.9%, Aldrich) in 1.0 M HCl (32%, Labchem) were initially subjected to ten charge/discharge cycles. From the measured charge/discharge cycles, the CE, VE, EE, discharge capacity, and capacity retention of the two electrolytes were compared. The best-performing electrolyte was then subjected to 100 charge/discharge cycles to assess the long-term performance of the electrolyte.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

Research data are not shared.

## Keywords

bismuth catalysts, hydrogen production, iron–chrome redox flow battery performances, open-circuit voltage

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