

# Revisiting the Cycling Stability of Ferrocyanide in Alkaline Media for Redox Flow Batteries

*Teresa Páez,<sup>[a,b]</sup> Alberto Martínez-Cuezva,<sup>[c]</sup> Jesús Palma,<sup>[a]</sup> and Edgar Ventosa<sup>[a,d,e]\*</sup>*

<sup>a</sup> IMDEA Energy, Avda. Ramón de la Sagra 3, E-28935 Móstoles, Madrid, Spain

E-mail: [eventosa@ubu.es](mailto:eventosa@ubu.es)

<sup>b</sup> Departamento de ingeniería Química Industrial y del Medio Ambiente, Escuela Técnica Superior de Ingenieros Industriales. Universidad Politécnica de Madrid, C/José Gutiérrez Abascal, 2, 28006, Madrid, Spain.

<sup>c</sup> Departamento de Química Orgánica, Facultad de Química, Regional Campus of International Excellence “Campus Mare Nostrum”, Universidad de Murcia, E-30100, Murcia, Spain

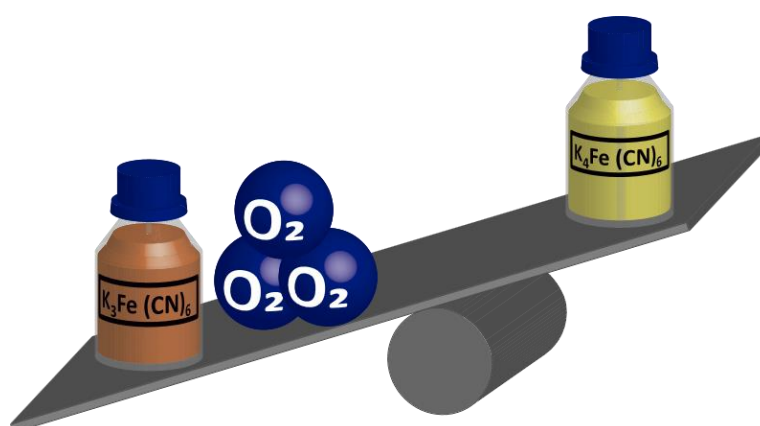
<sup>d</sup> Departamento de Química, Universidad de Burgos, Pza. Misael Bañuelos s/n, E-09001 Burgos, Spain

<sup>e</sup> International Research Centre in Critical Raw Materials-ICCRAM, University of Burgos, Plaza Misael Bañuelos s/n, E-09001, Burgos, Spain

## Abstract

In the quest for searching for new redox-flow battery chemistries, cycling stability must be carefully evaluated since it is one of the most important parameters of new active species. However, it is challenging to elucidate the intrinsic stability during operation of a redox flow battery. The symmetrical flow battery cell is a powerful tool that helps to unambiguously determine the cycling stability. Herein, trustworthiness of this technique is critically re-evaluated. Potassium ferrocyanide in alkaline media is used as a case study since i) it is the best performing species for the catholyte of alkaline flow batteries in terms of reversibility, solubility, costs and environmental compatibility and ii) the cycling stability of this species is still under strong debate. Potassium ferrocyanide is found to be stable at pH 14 upon electrochemical cycling when the oxygen evolution reaction is prevented, which should encourage researchers to resume the use of this species. The results also reveal that care should be taken when interpreting results from this powerful technique to avoid misleading conclusions.

## TOC GRAPHICS



**Keywords:** redox flow batteries; electrochemistry; stability; ferrocyanide; alkaline media

## 1. Introduction

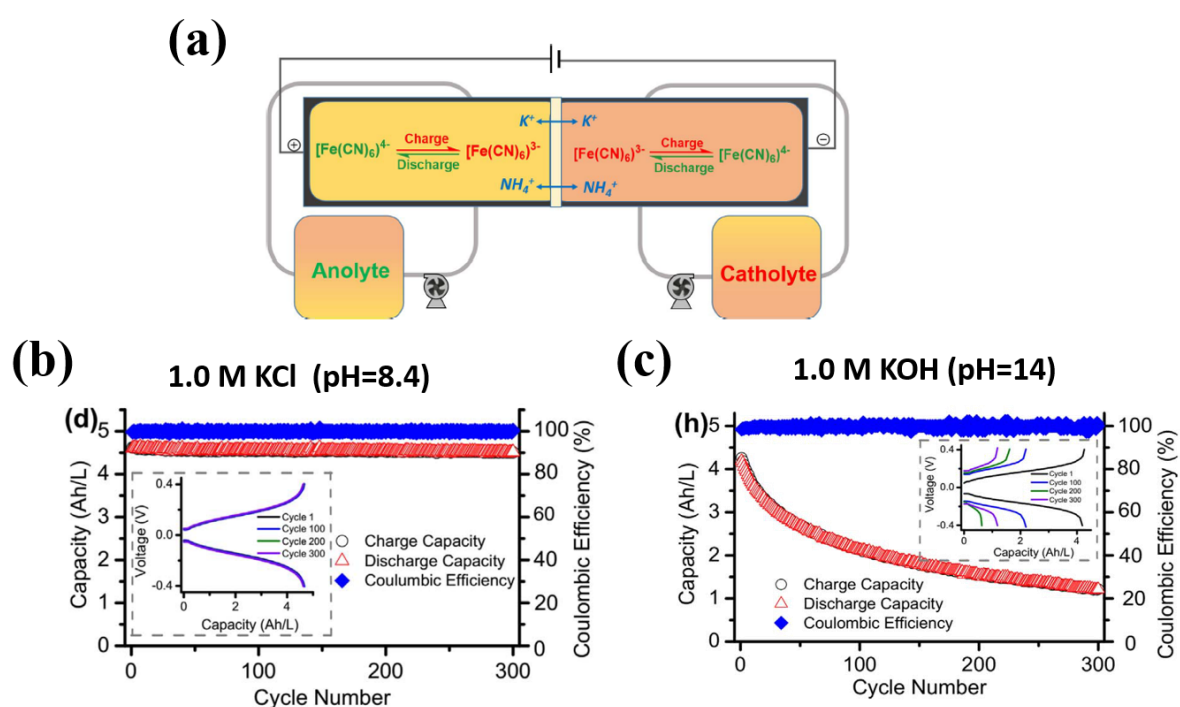
Energy storage technologies are considered to be a promising solution to deal with the challenge that the intermittent nature of renewable energy sources represents. Among various energy storage systems, redox flow batteries (RFB) have emerged as a suitable candidate for large applications due to their independent scalability of energy and power and their long cycle life[1]. To date, all-vanadium redox flow battery represents the most developed and commercialized RFB[2]. However, the use of vanadium electrolyte has several drawbacks, such as scarcity and corrosiveness[3], which has triggered the interest in finding alternative chemistries for RFB.

Alkaline flow batteries have attracted much attention as an alternative to vanadium electrolyte. All alkaline chemistries reported so far are based on the use of potassium ferrocyanide as active species in the positive compartment in combination with electroactive organic compounds in the negative one, including anthraquinone –  $K_4Fe(CN)_6$ [4],[5],[6], vitamin B- derivatives –  $K_4Fe(CN)_6$ [7], alloxazine –  $K_4Fe(CN)_6$ [8], phenazine-derivatives –  $K_4Fe(CN)_6$ [9],[10]. Since potassium ferrocyanide is the only material found to be active for the positive compartment, the intrinsic electrochemical properties of this species has become of high scientific interest.

Cycling stability is one of the most important parameters of the active species for redox flow batteries. However, it is challenging to elucidate the intrinsic stability during operation of a redox flow battery. Hydrogen evolution, species crossover through the membrane or degradation of the active species used in the opposite compartment are other sources of capacity fading, which hinder an unambiguous determination of the intrinsic cycling stability of an active species. Recently, the symmetrical flow battery cell was proposed to overcome this challenge and unambiguously evaluate the cycling stability of new redox flow battery chemistries (**Figure 1a**).[11][12][13] In this configuration, the same electrolyte in its oxidized and reduced form is used for the positive and negative compartment. In this way, other sources of capacity fading are avoided. Consequently, a symmetrical flow battery cell has been used to investigate the electrochemical stability of ferrocyanide at various pH [14]. The main conclusion of the study

was that ferrocyanide is not stable at strong alkaline media (pH = 14) releasing free CN<sup>-</sup> and causing a rapid capacity fading (**Figure 1b and 1c**). These results have generated an intensive debate in the community since several alkaline flow batteries based on ferrocyanide, e.g. Zn-Fe flow battery, have shown to deliver long cycle life.[15], [16]

Herein, we critically re-evaluate the symmetrical flow battery cell for stability tests of active species using the interesting study case of ferrocyanide in alkaline media. Two important conclusions are reached: I) The symmetrical flow battery cell is not a flawless tool for the evaluation of stability of electroactive species for redox flow battery. Although the symmetrical flow battery cell is a very useful tool, caution needs to be exercised when analyzing the results. II) The ferrocyanide in strong alkaline media (pH 14) is not unstable as previously proposed, which should re-encourage researches to resume their search for new alkaline flow battery chemistries based on it.



**Figure 1.** Cycling stability of ferricyanide/ferrocyanide conducted in a symmetrical flow battery cell at different pH conditions. (a) Schematic representation of a  $\text{K}_3\text{Fe}(\text{CN})_6 / \text{K}_4\text{Fe}(\text{CN})_6$  symmetrical redox flow battery cell. Capacity versus cycling number 0.2 M  $\text{K}_3\text{Fe}(\text{CN})_6 / \text{K}_4\text{Fe}(\text{CN})_6$  symmetrical cell (11-13 mL of electrolytes) in (b) 1.0 M KCl solution, and (c) 1.0 M KOH solution at  $40 \text{ mA/cm}^2$ . [14] Reproduced with permission from Elsevier.

## **2. Experimental Procedures**

### **Materials**

All chemicals were purchased from Sigma Aldrich and Alfa Aesar, and used as received.

### **Preparation of electrolytes**

In the symmetric flow cell, the catholyte was prepared by dissolving potassium ferrocyanide (98%, Alfa Aesar) in 1 M KOH (85 %, Sigma Aldrich) to afford 12 mL of 0.2 M ferrocyanide electrolyte. The anolyte was prepared by dissolving potassium ferrocyanide and potassium ferricyanide (99%, Alfa Aesar) in 1 M KOH to afford either 12 mL of 0.2 M ferricyanide electrolyte (balanced cell) or 45 mL of 0.1 M ferrocyanide + 0.2 M ferricyanide electrolyte (over size counter-compartment).

### **Flow battery cell**

Filter-pressed flow cell described elsewhere,[17]using Nafion 212, expanded graphite (SGL Carbon) and graphite felt (SGL Carbon) as the ion selective membrane, current collector and electrode, respectively, were used in this study. The projected area of the cell was 9 cm<sup>2</sup>. A peristaltic pump (MasterFlex L/S) was used to provide a flow rate of 50 mL min<sup>-1</sup>.

### **Electrochemical characterization.**

Galvanostatic charge-discharge measurements were conducted using a Biologic VMP multichannel potentiostat. The battery was galvanostatically cycled at  $\pm 20 \text{ mAcm}^{-2}$  with voltage limits of  $\pm 0.4 \text{ V}$ .

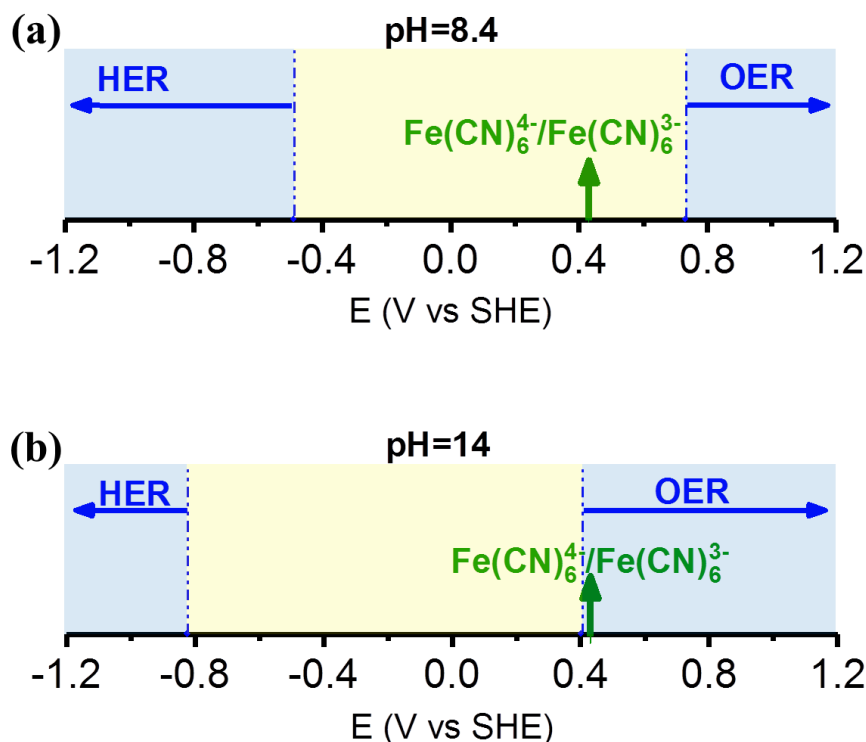
## **3. Results and Discussion**

### **3.1. Oxygen evolution reaction in alkaline media.**

One of the evident drawbacks of all aqueous-based batteries, including redox flow batteries, is the relatively narrow thermodynamic electrochemical stability window (1.23 V), which is limited by the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER).

The thermodynamic potential of OER and HER is strongly dependent on proton activity (Nernstian dependency) and, as a consequence, the pH of the electrolyte plays a fundamental role in processes associated with both reactions.

The HER at the negative electrode is kinetically faster than the OER, which in most batteries make the HER the limiting side reaction, [18] e.g. iron-chromium ( $E^0$  of  $\text{Cr}^{2+}/\text{Cr}^{3+} = -0.41$  V)[19] and all-vanadium ( $E^0$  of  $\text{V}^{2+}/\text{V}^{3+} = -0.26$  V).[19] Therefore, the use of a symmetrical cell for the study of catholytes avoids the HER enabling the deconvolution of chemical stability on the overall performance to a greater extent. When ferrocyanide is used as catholyte the HER does not occur in a symmetrical cell, which may conclude that electrolyte decomposition does not play an important role when evaluating the cycling stability of ferrocyanide in this cell configuration. However, the occurrence of the OER cannot be easily neglected, and should be considered. **Scheme 1** illustrates the thermodynamic stability window of the electrolyte at a pH 8.4 and pH 14 as well as the redox potential of ferrocyanide at these two values of pH. Obviously, the thermodynamic window ( $E_{\text{OER}} - E_{\text{HER}}$ ) does not change with pH, but the absolute potentials shift towards lower values as the pH increases. However, the redox potential of potassium ferrocyanide is not dependent on the pH, but it is on the activity of potassium cations. If 1 M KCl is used in neutral pH, for maintaining a good ionic conductivity, the redox potential of the ferrocyanide will not vary significantly ( $E_{\text{Ferro/Ferri}}(1 \text{ M KOH}) \approx E_{\text{Ferro/Ferri}}(1 \text{ M KCl}) \approx 0.42 \text{ V vs SHE}$ ). As a result, the redox potential of ferrocyanide at pH=8.4 will be within the stability window of the electrolyte (330 mV below the potential of the OER), while the potential of both reactions (ferrocyanide and the OER) will overlap in alkaline media. Thus, it is safe to neglect the occurrence of the OER during electrochemical cycling of ferrocyanide at neutral pH, but it cannot be ruled out in alkaline media.



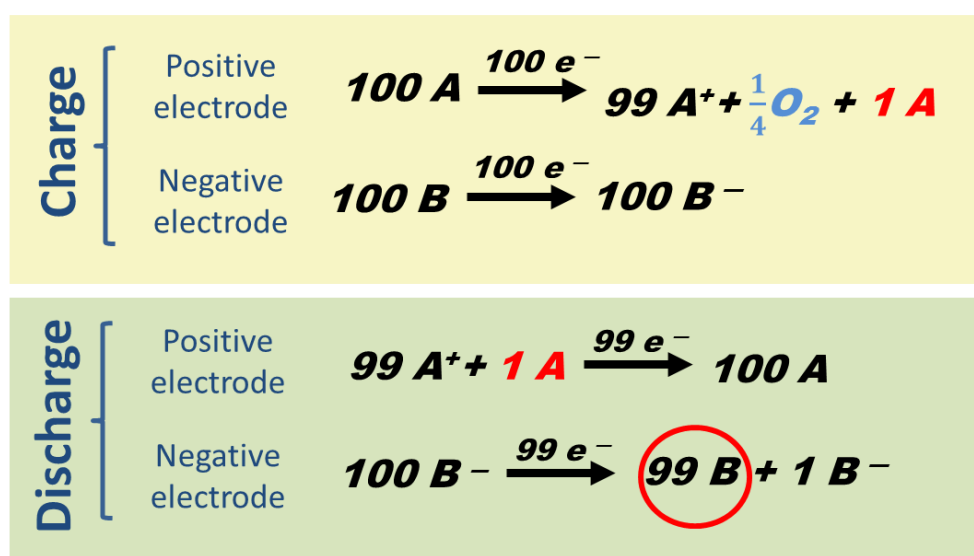
**Scheme 1.** Schematic illustration of the pH dependency of the stability window in aqueous media with respect to the pH independent behaviour of potential of ferrocyanide for (a) neutral media, (b) alkaline media. In pH 8.4 media, potential of the couple  $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$  will be within the electrochemical stability window, while in pH 14 media, it will be on the boundary of the OER.

### 3.2. Capacity unbalancing of a battery triggered by side reaction.

Irreversible side reactions such as the OER lead to specific capacity unbalance between positive and negative electrode. **Scheme 2** illustrates the general mechanism of capacity unbalancing by the OER during a charge/discharge cycle. The positive electrode suffering a side reaction will not be fully charged (99 %) as some electrons (1 %) are consumed by the parasitic reaction, while the negative electrode will be able to be fully charged (100 %). During the discharge process, the positive electrode will be the limiting electrode since it was not fully charged. As a result, the discharge capacity of the battery will be limited to 99 % of its capacity. Most importantly, in the subsequent charge process, the negative electrode will not start from a fully discharge state (100 % - 99 % = 1 %). Consequently, the battery will not be able to be fully charged in the subsequent charge process since only 99 % of the species in the negative

electrode are in its discharge state and the battery will have lost this 1 % of its charge storage capacity. If a side reaction is occurring during charge/discharge of the species of interest, the capacity unbalancing will be accelerated when using an alkaline ferrocyanide - ferricyanide symmetrical flow. The accelerated fading is due to the fact that the side reaction not only will occur in one electrode, but it will occur in both electrodes (in one electrode during charge and in the another one during discharge). As a result, the capacity fading will be accelerated by a factor of 2.

In the case of ferrocyanide, it was discussed above that the OER will likely not occur in neutral pH. The question is whether it takes place at pH 14. Thermodynamically, the OER might occur but it is kinetically very sluggish. However, the OER might be promoted by several factors (or combination of them), e.g. presence of electrocatalysts in the electrode that improves the kinetics of the OER, small current densities that promote the kinetically slow reaction or large operating overpotentials derived from a high internal resistance (membrane, felts, flow factor, etc) that increases the driving force for the OER.



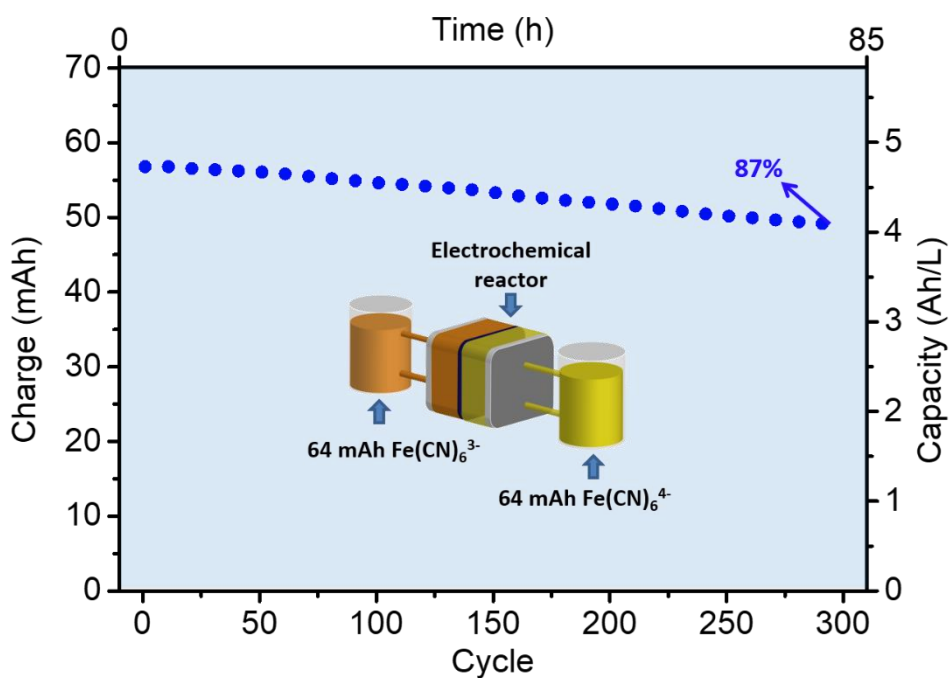
**Scheme 2.** Schematic illustration of the concept of battery unbalance by the OER in aqueous flow batteries during a charge-discharge cycle.

### 3.3. Cycling stability of a ferrocyanide electrolyte at pH 14 in a symmetrical flow cell.

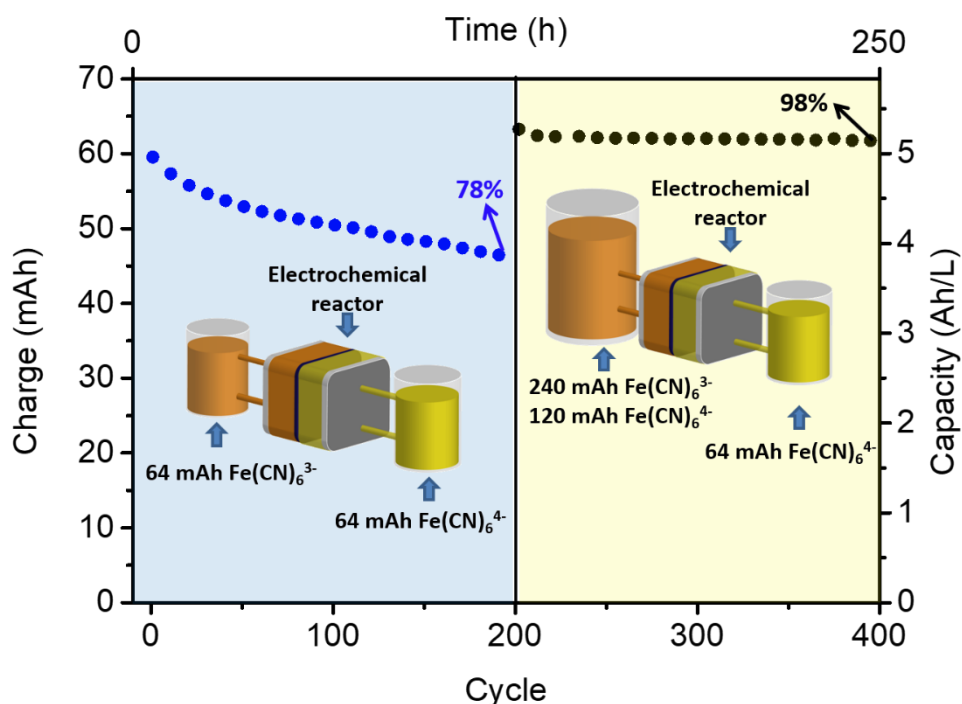


A symmetrical flow cell containing a balanced amount of ferro- and ferricyanide was used for an easy evaluation of ferrocyanide cycling stability at pH 14. Thus, 0.2 M ferrocyanide and 0.2 M ferricyanide dissolved in a 1 M KOH aqueous solution are used as electroactive species for the positive and negative compartment, respectively. A shadow capacity fading was observed during the 300 cycles and 90 hours of the test (**Figure 2**), retaining 87 % of its initial charge capacity. Although the capacity retention is not outstanding, this value is drastically better than the capacity retention previously reported in alkaline media using symmetrical cell[14], in which the retention dropped below 50 % after only 100 cycles. This discrepancy clearly shows that the symmetrical flow cell is not flawless and there must be some other factors that are not been considered. As above-mentioned, battery unbalancing due to the OER could be responsible for capacity fading. Although both experiments, the previously reported and the one reported here, were carried out at the same conditions (current density, flow rate), there are factors which are very difficult to control. We notice that the overpotentials in our experiments are significantly lower than that of the previous report, which lead us to propose the OER as the source of the discrepancies. To corroborate this hypothesis, an identical symmetrical flow cell was cycled under favorable conditions for the OER, i.e. the graphite felts were intentionally contaminated with an OER electrocatalyst (Ni(OH)<sub>2</sub> particles)[[20], [21], [22]] and was cycled at lower current density (20 mA cm<sup>-2</sup> instead of 40 mA cm<sup>-2</sup>) to promote the kinetically slower process (the OER), as it occurs in all-vanadium flow batteries with the HER. **Figure 3** shows the first 200 cycles for an initially balanced symmetrical flow cell (64 mAh of reversible charge for each compartment). The capacity retention after 200 cycles was 78 %, which confirms the accelerated fading under favorable conditions for the OER. Thus, side reactions cannot be rule out when evaluating the cycling stability using a symmetrical flow cell. In the particular case of ferrocyanide, the strong capacity fading previously reported appears to be related to the OER occurring under those experimental conditions, and it does not represent a general behavior in alkaline media. However, our experiment can neither confirm nor rule out that ferrocyanide is

completely stable in alkaline media. It should be noted that the OER would occur in both compartments since they are symmetrical, so that the occurrence of the OER in this configuration cannot be determined by analyzing the coulombic efficiency (Fig S1 and S2). To be able to attribute the capacity fading to the OER (charge unbalancing) or degradation of the active species, we applied the following strategy for symmetrical flow batteries, which allows one to deconvolute the contribution of the cell unbalancing due to the occurrence side reactions and degradation of the active species. After 200 cycles, the experiment was paused. The volume of one compartment and thus, the amount of active species and charge storage capacity, was significantly increased so that the other compartment became the limiting side. In this way, the electrochemical results can be only attributed to the limiting compartment, which become the “working compartment”, while the large compartment acts as “counter-compartment”. Since the cell was already unbalanced after 200 cycles, species in both oxidized and reduced states were present in the working-compartment. Thus, species in both oxidized and reduced states were added to the counter-compartment, so that a full “rebalancing” of the working compartment could be possible. **Figure 3** shows that the initial capacity was recovered in the cycle 201, which clearly demonstrates that the capacity fading was completely due to the occurrence of the OER. Indeed, the capacity fading in the subsequent 200 cycles (200 – 400 cycle) using a large excess of active species in the counter-compartment was drastically reduced (98 % retention). Actually, the first 10 cycles after the “rebalancing” (201 – 211) accounted for 1 % of the capacity fading so that a capacity retention of 99 % was archived in the last 190 cycles (ca. 120 h), delivering  $5.15 \text{ Ah L}^{-1}$  out of the theoretical value of  $5.36 \text{ Ah L}^{-1}$  after 400 cycles (material utilization of 96 %), which are as high as other values previously reported in neutral pH.[14] The use of large counter-reservoir with both oxidized and reduced species also enable a higher utilization rate since changes in the redox potential of the electrolyte of that compartment are less pronounced (extreme state of changes are avoided). As a consequence, the effective cut-off potential of the working compartment is increased.



**Figure 2.** Evaluation of charge capacity of a ferrocyanide symmetrical flow cell at pH 14. The cycling stability study was performed at  $40 \text{ mA cm}^{-2}$  using 12 mL of 0.2 M  $\text{K}_3\text{Fe}(\text{CN})_6$  and 12 mL of 0.2 M  $\text{K}_4\text{Fe}(\text{CN})_6$  in 1M KOH solution for each compartment.



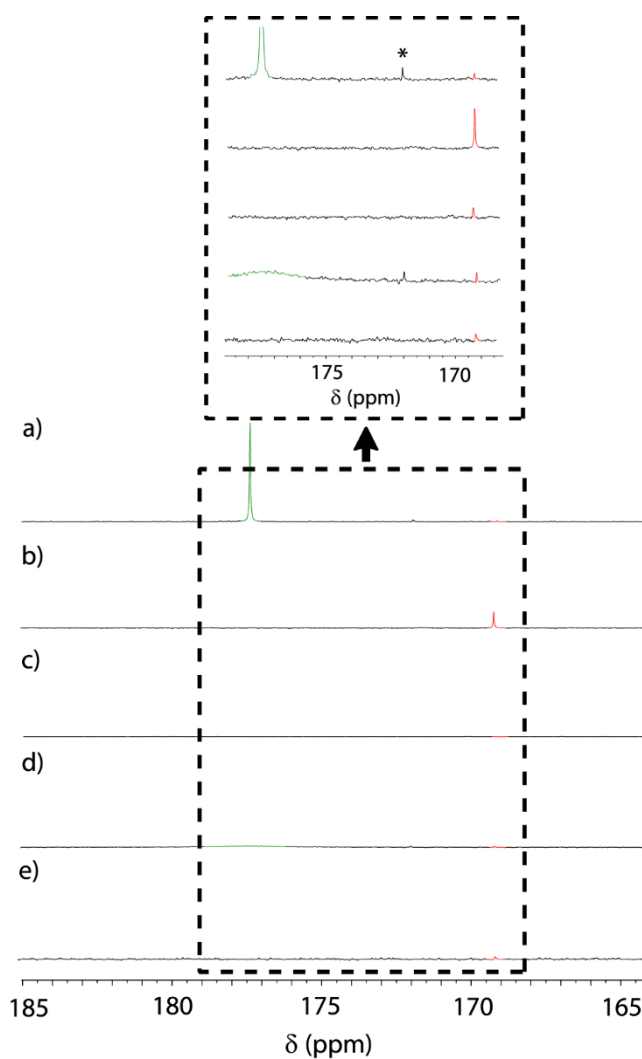
**Figure 3.** Evaluation of charge capacity of a ferrocyanide symmetrical flow cell at pH 14. The cell was intentionally contaminated with OER electrocatalyst ( $\text{Ni}(\text{OH})_2$ ) to promote the charge unbalancing. The cycling stability study was performed at  $20 \text{ mA cm}^{-2}$  using 12 mL of 0.2 M  $\text{K}_3\text{Fe}(\text{CN})_6$  and 12 mL of 0.2 M  $\text{K}_4\text{Fe}(\text{CN})_6$  in 1M KOH solution for each compartment. After 200 cycles, the electrolyte of one compartment was exchanged for a larger volume of electrolyte (45 mL) containing both ferri- and ferrocyanide species (0.1 M  $\text{K}_3\text{Fe}(\text{CN})_6$  and 0.2 M

$\text{K}_4\text{Fe}(\text{CN})_6$ ). The large excess of active species in the fresh compartment makes the another compartment acts as working compartment for the last 200 cycles.

### 3.4. $^{13}\text{C}$ -NMR post mortem analysis of the ferrocyanide electrolyte.

The decomposition of ferrocyanide in alkaline media upon electrochemical cycling has raised concerns since it was proposed that cyanide anions are released.[14] The recovery of the initial charge capacity after 201 cycles (**Figure 3**) is an indirect evidence that ferrocyanide does not decompose since it remains electrochemically active. Nevertheless,  $^{13}\text{C}$ -NMR post mortem analysis was carried out to shed light into this issue. The  $^{13}\text{C}$ -NMR spectrum of a fresh electrolyte containing 0.2 M  $\text{K}_4\text{Fe}(\text{CN})_6$  in 1 M KOH shows the expected signal of ferrocyanide at 177 ppm (**Figure 4a**). After 400 cycles, the signal at 177 ppm disappeared, emerging a signal at 169 ppm (**Figure 4b**), which is consistent with the previous report.[14] The changes in the  $^{13}\text{C}$ -NMR spectra were attributed to the decomposition of ferrocyanide resulting in the release of free cyanide anions. However, this hypothesis is not supported by our electrochemical results leading us to explore alternative explanations. Actually, there are two important facts which must be considered: I) The ferricyanide anion is a paramagnetic species so that it is not detected using standard NMR equipment.[23] **Figure 4c** shows the  $^{13}\text{C}$ -NMR of a 0.2 M  $\text{K}_3\text{Fe}(\text{CN})_6$  in 1 M KOH, where any carbon signal related to the ferricyanide appeared. In fact, it was observed that the presence of small amounts of ferricyanide blocks the carbon signal from the ferrocyanide as shown in **Figure 4d** (0.19 M  $\text{K}_4\text{Fe}(\text{CN})_6$  + 0.01 M  $\text{K}_3\text{Fe}(\text{CN})_6$ ). II) The employed KOH contains a large amount of impurities (85 wt% purity is typically used at lab scale, which was also used here), which includes  $\text{K}_2\text{CO}_3$ . **Figure 4e** shows the  $^{13}\text{C}$ -NMR spectrum of a fresh 1 M KOH solution. The signal of the  $\text{CO}_3^{2-}$  species appeared at a similar chemical shift as expected for the free cyanide anion ( $\delta = 169$  ppm). Considering all these facts, the following explanation is proposed. The battery unbalancing occurs due to the OER during electrochemical cycling results in the presence of ferricyanide at the end of the experiment. The paramagnetic properties of the ferricyanide suppresses the signals from both ferrocyanide and

ferricyanide species at the NMR spectra, which does not mean that these active species decompose as indicated from the electrochemical data (**Figure 3**). The signal attributed to the presence of free cyanide anions likely is in fact originated from the  $\text{CO}_3^{2-}$  anions present in the media. Thus, our interpretation of the  $^{13}\text{C}$ -NMR analysis does not involve the decomposition of the ferrocyanide, consistent with our electrochemical evidence.



**Figure 4.** Partial  $^{13}\text{C}$ -NMR spectra (100 MHz, 90:10  $\text{H}_2\text{O}+\text{D}_2\text{O}$ , 298 K) of: a) 0.2 M  $\text{K}_4\text{Fe}(\text{CN})_6$  in an aqueous solution of 1M KOH; b) 0.2 M  $\text{K}_4\text{Fe}(\text{CN})_6$  in an aqueous solution of 1 M KOH after 400 electrochemical cycles; c) 0.2 M  $\text{K}_3\text{Fe}(\text{CN})_6$  in an aqueous solution of 1M KOH; d) 0.19 M  $\text{K}_4\text{Fe}(\text{CN})_6$  + 0.01 M  $\text{K}_3\text{Fe}(\text{CN})_6$  in an aqueous solution of 1M KOH; e) aqueous solution of 1M KOH. Inset: Amplification of the signals.  $\text{K}_4\text{Fe}(\text{CN})_6$  signals (red colour); residual  $\text{CO}_3^{2-}$  (red colour); The purity of KOH was 85 wt.% as typically used for lab scale alkaline flow batteries; \* unknown compound.

#### 4. Conclusions

In summary, the symmetrical flow battery cell is re-evaluated in this study as a tool for studying the intrinsic cycling stability of active species for redox flow batteries. In particular, the influence of parasitic side reactions during electrochemical cycling in the apparent fading of the active material is discussed. The study case of ferrocyanide in alkaline media is used as an example of possible misinterpretation of the results of this powerful tool. This case was selected due to its tremendous implications in the field of energy storage as it is the only active species known for the positive compartment of alkaline flow batteries. In this system, the occurrence of OER cannot be ruled out so that the impact of this parasitic side reaction in the cell unbalancing and capacity fading must be taken into account. It is demonstrated that the promotion of the OER by adding an OER electrocatalyst accelerates the capacity fading, which confirms that the unbalancing due to the OER plays an important role. By oversizing one compartment after 200 cycles, the initial capacity is recovered, indicating that ferrocyanide does not lose electrochemical activity, but the capacity fading is completely due to the cell unbalancing. After 400 cycles (250 h), the symmetrical cell still delivers a volumetric capacity of  $5.16 \text{ Ah L}^{-1}$ , which represent a materials utilization of 96 % (theoretically  $5.36 \text{ Ah L}^{-1}$ ). Thus, ferrocyanide is not highly unstable at strong alkaline media ( $\text{pH} = 14$ ) putting in doubt the release of free-CN ions from the ferro / ferri cyanide ions previously proposed.

The symmetrical flow cells are undoubtedly a powerful tool to investigate the intrinsic cycling stability. However, this does not mean that they are faultless. Misinterpretation of the results might lead to drastic changes in research direction. In the case of ferrocyanide, researchers were discouraged to use it in alkaline media which has slowed down the development of alkaline flow batteries. Hopefully, the results presented here will attract the attention of the scientific community back to high pH values, as it has significant advantages at industrial scale, e.g. corrosion.

## **ASSOCIATED CONTENT**

## Supporting Information

Coulombic and energy efficiencies of the cells can be found in the supporting information.

## Notes

The authors declare no competing financial interest.

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