

Flow electrode capacitive deionization with iron-based redox electrolyte

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HIGHLIGHTS

- Low-cost iron-based redox couples outperformed typical activated carbon FCDI.
- The concentration of iron chloride influences the salt removal rate.
- 0.2 M of iron chloride double the desalination compared to activated carbon.
- Iron chloride in flow electrode decreases the pH of diluate and concentrate streams.
- Iron citrate increases desalination by 23 %, and the water product has a pH around.

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ABSTRACT

Flow electrode capacitive deionization (FCDI) employs carbon-based materials for electrochemical separation. Redox additives like vanadium, ferricyanide, and organic molecules have boosted desalination rates in FCDI. However, these additives must be low-cost, have chemical stability in electrolytes, and have low toxicity. We investigate two iron-based redox couples, iron chloride, and iron citrate, for their cost-effectiveness and reduced health risks. We incorporate them with activated carbon (AC) in flow electrodes, resulting in a significant enhancement of the salt removal rate, with iron chloride increasing it by 100 % and iron citrate by 23 % compared to standard AC slurries. In our system, the AC exhibits a salt removal rate of $7.8 \mu\text{mol cm}^{-2} \text{ min}^{-1}$, while the iron chloride system reaches $15.6 \mu\text{mol cm}^{-2} \text{ min}^{-1}$. Iron citrate flow electrodes achieve a desalination rate of $9.6 \mu\text{mol cm}^{-2} \text{ min}^{-1}$, maintaining a pH suitable for potable water. We observe that iron chloride concentration in the flow electrode influences iron crossover and pH in the water streams, leading to acidity. Conversely, the iron citrate-based slurry maintains minimal iron crossover and a neutral pH. This study highlights iron-based redox additives as promising for FCDI slurries and the need for tailored flow electrode composition based on specific ion removal requirements.

1. Introduction

Water resource management is a significant concern in a context where scarcity is predicted to grow over time. Therefore, water treatment for potable water production, water recycling in industrial processes, or recovering valuable ions is relevant. In this context, electrochemical processes have attracted interest recently due to the possibility of treatment of different feedwater compositions and their

energy efficiency.

Among those techniques, electrodialysis (ED), capacitive deionization (CDI), flow-electrode capacitive deionization (FCDI), and redox-flow desalination (RFD) are the most investigated processes. However, CDI is limited to treating low salt concentration streams due to the limitation of salt adsorption capacitive at the electrodes. Electrodialysis is a mature technology, and it is considered to be more efficient in salt concentrations lower than 3 g L^{-1} of salt.

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RFD and FCDI are based on flow electrodes but with distinguished compositions and working principles. While RFD is based on the redox flow batteries architecture, it operates with flow electrodes based on soluble redox couples that are oxidized and reduced in the electrodes. On the other hand, in FCDI, the flow electrodes consist of a slurry, where the active materials are commonly based on carbon materials, such as activated carbon (AC), carbon black (CB), graphene, and carbon nanotubes (CNT). The current collector charges the materials, which in turn electro-adsorb ions from the electrolyte. As the electrons are transported via the physical contact of the particles on the current collector or via the charge transfer between the slurry particles, the resistance of the flow electrode in FCDI is high. Some studies tried to improve the flow electrode by increasing the solid content or mixing different carbon materials. However, those strategies increase the chance of clogging, the pumping energy, and the cost of flow electrodes.

Recently, a new strategy to improve conductivity in the flow electrode involved mixing the carbon particles with redox couples. Several inorganic redox couples such as $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ [1–3], $\text{V}_2^+/\text{V}_3^+$ [4], I^-/I_3^- [5], and organic redox couples such as sodium anthraquinone - 2 - sulfonate (AQS), 4 - hydroxy - 2,2,6,6 - tetramethylpiperi - dine 1 - oxyl (TEMPO), and hydroquinone $\text{H}_2\text{Q}/\text{Q}$ [3]. Among those redox couples, $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ is the most applied reactant due to its fast electrochemical kinetics and accessibility. However, this redox couple reacts with several transition metals, such as iron, copper, nickel, manganese, and zinc, and co-precipitate, forming solid particles known as Prussian Blue Analogs. These precipitates will likely foul the membrane, hindering their application in real applications. The species $\text{V}_2^+/\text{V}_3^+$ and I^-/I_3^- can be toxic in water environments, and vanadium salts are also expensive chemicals. Furthermore, organic redox couples are usually expensive, have limited water solubility, and also offer environmental risks. Iron-based flow electrodes can be an interesting alternative to those reactants, as iron is a ubiquitous element with several non-costly salts. Iron can also be complexed with organic molecules in a variety of complexes, allowing various compounds to be investigated. Studies have reported the use of iron diethylenetriamine pentaacetate DPTA [6] and iron citrate (Fe – Cit) [7] for RFB, and iron malonate [8] with and without CNTs in the flow electrode. Those studies suggest a low energy consumption and high productivity of water purification.

Here, we propose the application of iron chloride (Fe – Cl) and Fe – Cit as flow electrodes in a typical FCDI cell. The desalination performance of those redox couples with and without AC is evaluated. The aim is to determine if those redox couples can improve the salt removal in FCDI cells and determine the concentration's effect on the performance. It is shown that even the lowest concentration of Fe – Cl in this study (0.05 M) has a better desalination rate than typical FCDI slurries with 15 wt% of AC. Depending on the concentration, the salt removal rate can increase with the additives two-fold, indicating the possibility of enhancing FCDI productivity with iron-based salts. Based on the results, it is demonstrated that both redox couples are interesting alternatives for flow electrodes, and the choice of the appropriate composition of the flow electrode should be tailored to the specific application.

2. Experimental

2.1. Materials

The feedwater was prepared with NaCl (Carl Roth chemicals, 99.5 %). Activated carbon (Carbopal SP11), iron (III) chloride hexahydrated (Carl Roth chemicals, 99.0 %), iron (II) chloride tetrahydrated (Carl Roth chemicals, 99.0 %), and sodium citrate tribasic (Sigma-Aldrich, 99.0 %) were used for the preparation of the flow electrodes. The activated carbon was characterized in a previous study. The BET surface area of the AC was found to be $950 \text{ m}^2 \text{ g}^{-1}$, and particle size d_{90} and d_{50} equal to 64 and $16 \mu\text{m}$, respectively. Also, typical optical microscopic pictures of the AC are shown in the study of Rommerskirshen

and co-workers [9].

2.2. FCDI cell configuration

The FCDI experiments were performed with the same cell design described in a previous work [10]. The FCDI cell was set up in the so-called single-module (SM) configuration. In this way, the flow electrode has one reservoir, and the slurry recirculated through the current collectors, as shown in the scheme in Fig. 1. The cell consisted of two acrylic end plates and two epoxy-impregnated graphite current collectors (Müller & Rössner GmbH & Co. KG) with 3 mm in width and 2 mm in-depth carved flow channels. Two 0.5 mm mesh spacers (Fumatech BWT GmbH, ED-40) were used as a water channel between the membranes, one spacer being the diluate channel and the other being the concentrate one.

Cation and anion exchange membrane: Fumasep FKB-PK-130 and Fumasep FAB-PK-130, respectively (Fumatech BWT GmbH), were applied in the system. The cell used three membranes, and the configuration depended on the charge iron complexes evaluated. To avoid the diffusion of the redox couples from the flow electrode to the water channels when the iron complex had a positive charge (Fe – Cl flow electrode), an anion-cation-anion exchange membrane (ACA) configuration was used. Conversely, when the iron complex had a negative charge (Fe – Cit), the cell was assembled in a cation-anion-cation exchange membrane (CAC).

A peristaltic pump (Ismatec Reglo ICC, Cole-Palmer) was used to supply water to the FCDI cell, and a pump (MasterFlex Easyload II Dual Channel) was used to pump the flow electrodes. A power supply (Keysight Agilent E3644A) was used to control the applied voltage in the FCDI cell. The conductivity of the product solution was monitored with conductivity probes (Knick SE 615/1-MS, Knick Elektronische Messgeräte GmbH & Co. KG), and the chloride and sodium content of the diluate and concentrate was determined by high-performance liquid chromatography (Agilent 1200, HPLC).

2.3. Synthesis of iron-based electrolytes

This study investigated two iron complexes: iron chloride (Fe–Cl) and iron citrate (Fe–Cit). The iron chloride flow electrodes were prepared by mixing equimolar quantities of iron chloride (III) and iron chloride (II) and dissolving the salts in deionized water. The total iron concentration Fe_T was 0.05, 0.1, 0.2, and 0.4 M, and NaCl was added in the electrolyte, so the flow electrode has the same concentration of NaCl (5 g L^{-1}) as the feedwater channels. The iron citrate solution consisted of an iron/citrate ratio of 1:3, with a total iron concentration of 0.2 M. For the synthesis of iron citrate (Fe–Cit), equimolar quantities of iron(III) chloride and iron(II) chloride were dissolved in deionized water along with NaCl (the equivalent of 5 g L^{-1}). In another beaker, sodium citrate was dissolved in deionized water and then mixed with the iron chloride solution. There was no adjustment of the electrolyte pH for the iron chloride and iron citrate experiments. In all experiments, the total electrode volume was 100 mL. In the experiments with activated carbon, it was added to make a 15 wt% of solids slurry, and the particles were kept in suspension by continuously stirring the flow electrode with a magnetic stirrer.

The crossover of iron to the water streams was analyzed by ICP-OES (PlasmaQuant PQ9000 Elite, Analytik Jena), and the citrate crossover was investigated by measuring the total organic carbon with a Total Organic Carbon Analyzer (Shimadzu Europa GmbH, Duisburg, Germany).

2.4. Desalination experiments

The desalination experiments were carried at a constant voltage of 1.2 V. The feedwater of diluate and concentrate channel consisted of

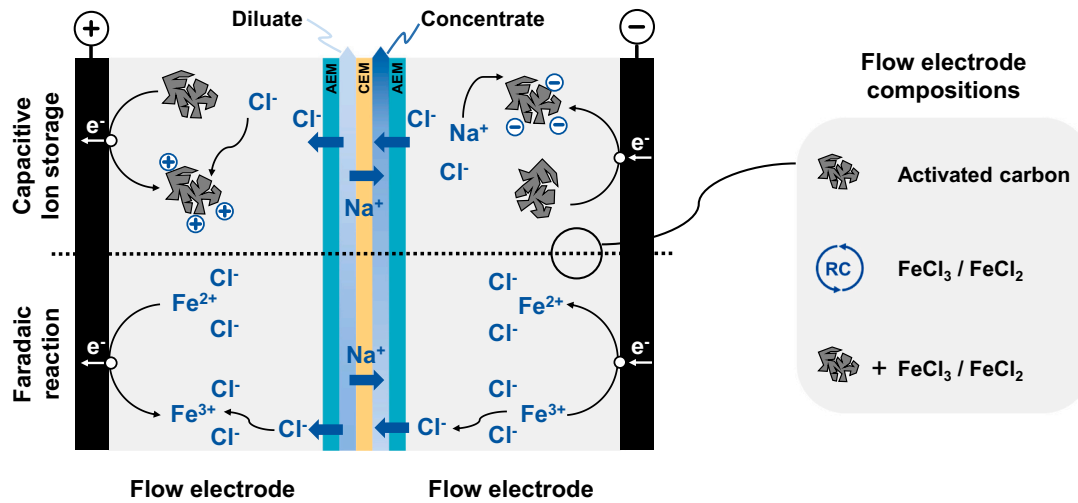


Fig. 1. Scheme of the FCDI cell used for the experiments. The flow electrodes are set up in the single-module configuration. The feedwater is in a single-pass mode, so the cell was continuously supplied with a new electrolyte. In the flow electrode, activated carbon particles adsorb ions with opposite charges in the cathode and anode compartments. The Fe^{3+} is reduced in the cathode to Fe^{2+} , and anions move from the flow electrode to the concentrate channel. On the anode side, the Fe^{2+} is oxidized to Fe^{3+} , and anions cross the membrane from the diluate to the flow electrode.

5 g L^{-1} of NaCl in the feed water, which is equivalent to 0.086 M of salt. The water pH in the feed was not modified and was around 5.6 to 5.8. The flow rate of diluate and concentrate was 5 mL min^{-1} , meaning the water recovery (WR), given by Eq. 1, was 50 % for all tests (where Q_d and Q_c are the diluate and concentrate flow rate).

$$WR = \frac{Q_d}{Q_d + Q_c} \quad (1)$$

We first investigated the FCDI cell in experiments with AC-only, Fe – Cl-only, and a mixture of Fe – Cl and AC. The composition of the flow electrodes and the parameters chosen for the desalination experiments are summarized and shown in Table 1.

In the experiments with Fe – Cl, the same parameters described for Fe – Cl were applied. However, the flow electrodes were investigated with only 0.2 M of Fe_2 , with and without AC.

2.5. Analysis of desalination performance

The performance of the desalination experiments was analyzed using the applied cell voltage, the electrical current, the flow rate of feed water, and the salt concentration of product water. The average salt removal rate (ASRR, $\mu\text{mol cm}^{-2}\text{min}^{-1}$) was calculated according to Eq. 2.

$$ASRR = \frac{(C_0 - C_t) \cdot V_s}{t \cdot A_{eff}} \quad (2)$$

where C_0 is the concentration of Na^+ in the feedwater and C_t is the salt concentration of the product water (mol L^{-1}) at a given time t . V_s is the total volume of treated water during time t , and A_{eff} is the membrane area in contact with the flow electrode. The charge efficiency (CE) is the ratio of charge transported by ions to the total electrical charge introduced into the system, as shown in Eq. 3.

$$CE = \frac{z \cdot F \cdot (C_0 - C_t) \cdot V_s}{\int idt} \quad (3)$$

where F is the Faraday constant ($96,485 \text{ C mol}^{-1}$), z is the equivalent number of electrons per mol of ions removed, M_{salt} is the molar mass of Na^+ , and dt is time. The volumetric energy consumption (E_{vol} , kWh m^{-3}) per volume of effluent for desalination can be calculated as follows in Eq. 4.

$$E_{vol} = \frac{\int idt \cdot V}{V_s} \quad (4)$$

where V is cell voltage, which was 1.2 V for all experiments. The energy consumption per mol of removed salt (E_{mol} , kJ mol^{-1}) was calculated by Eq. 5.

$$E_{mol} = \frac{\int idt \cdot V}{(C_0 - C_t) \cdot V_s} \quad (5)$$

3. Results and discussion

3.1. Comparison of desalination with iron chloride and AC-only flow electrodes

This section compares flow electrodes with several concentrations of Fe – Cl and a typical FCDI AC flow electrode. The experiments were run at a constant voltage of 1.2 V to avoid the reduction and oxidation of water. For the flow electrode with only AC, the system typically works as FCDI cells, where the AC particles touch the current collector and become charged. Then, the AC adsorbs the ions with opposite charges in the flow electrodes, and ions cross the membrane to balance the charge. For the system consisting of $\text{FeCl}_3/\text{FeCl}_2$ redox couple, the FeCl_2^+ and FeCl^+ (the predominant Fe^{3+} and Fe^{2+} species) are oxidized and reduced, according to Eq. 6 and Eq. 7, respectively.

Anodic reaction:

Table 1

Overview of the flow electrode compositions and FCDI system parameter settings for desalination experiments with iron chloride and activated carbon.

Composition			Flow electrode							
AC	(wt%)	0	0	0	0	15	15	15	15	15
Fe_{Total}	(mol L^{-1})	0.05	0.1	0.2	0.4	0	0.05	0.1	0.2	0.4



Cathodic reaction:



In this way, the reduction reaction creates an excess of negative charge at the cathodic side, and Cl^- must cross the anion exchange membrane (AEM) from the flow electrode to the concentrate channel, as shown in Fig. 1. Conversely, the oxidation reaction creates a positive charge excess on the anodic side, and Cl^- crosses the AEM from the diluate channel to the flow electrode. The results of desalination currents of flow electrodes with several Fe – Cl concentrations and a typical FCDI AC slurry are shown in Fig. 2a.

In Fig. 2a, the start of the experiment (0 min) was considered after 3 min of the power supply was turned on. In this way, the current peak that appeared at the experiments' start was removed, making the plots clearer. The current response for the flow electrode with AC was around 298 mA, and remained almost constant over 180 min of the experiment. Regarding the Fe – Cl flow electrodes, the current in the cell was higher for all iron concentrations than the AC flow electrode. For the 0.05, 0.10, 0.20, and 0.40 M of Fe_T , the average current for the experiments was 327, 451, 534, and 619 mA, respectively. Thus, for 0.05, 0.10, 0.20, and

0.40 M, the improvement relative to AC flow electrode was around 10, 51, 79 and 108 %.

The enhanced current for the Fe – Cl system is due to the facile charge transfer in the flow electrode, as the cell works like so-called redox flow desalination systems [2] or redox-mediated electrodialysis [1]. The Fe–Cl species oxidized at the anode are later reduced at the cathode and vice-versa, as the Fe–Cl species are recirculated in the current collectors, as shown in Eq. 6 and Eq. 7. The Nernst equation gives the anodic and cathodic electrochemical potential of the half-cell reactions, as represented in Eq. 8 and Eq. 9, respectively.

$$E_a = 0.77V - 0.059V \times \frac{[\text{FeCl}_2^+]}{[\text{FeCl}^+]} \quad (8)$$

$$E_c = 0.77V - 0.059V \times \frac{[\text{FeCl}^+]}{[\text{FeCl}_2^+]} \quad (9)$$

The difference between the anode potential, E_a , and the cathode potential, E_c gives the overall thermodynamical potential for the reaction. Since the standard potential E° of the anodic and cathodic reactions is the same, these terms cancel each other. Additionally, under the assumption that the activities of FeCl_2^+ and FeCl^+ are equal (considering

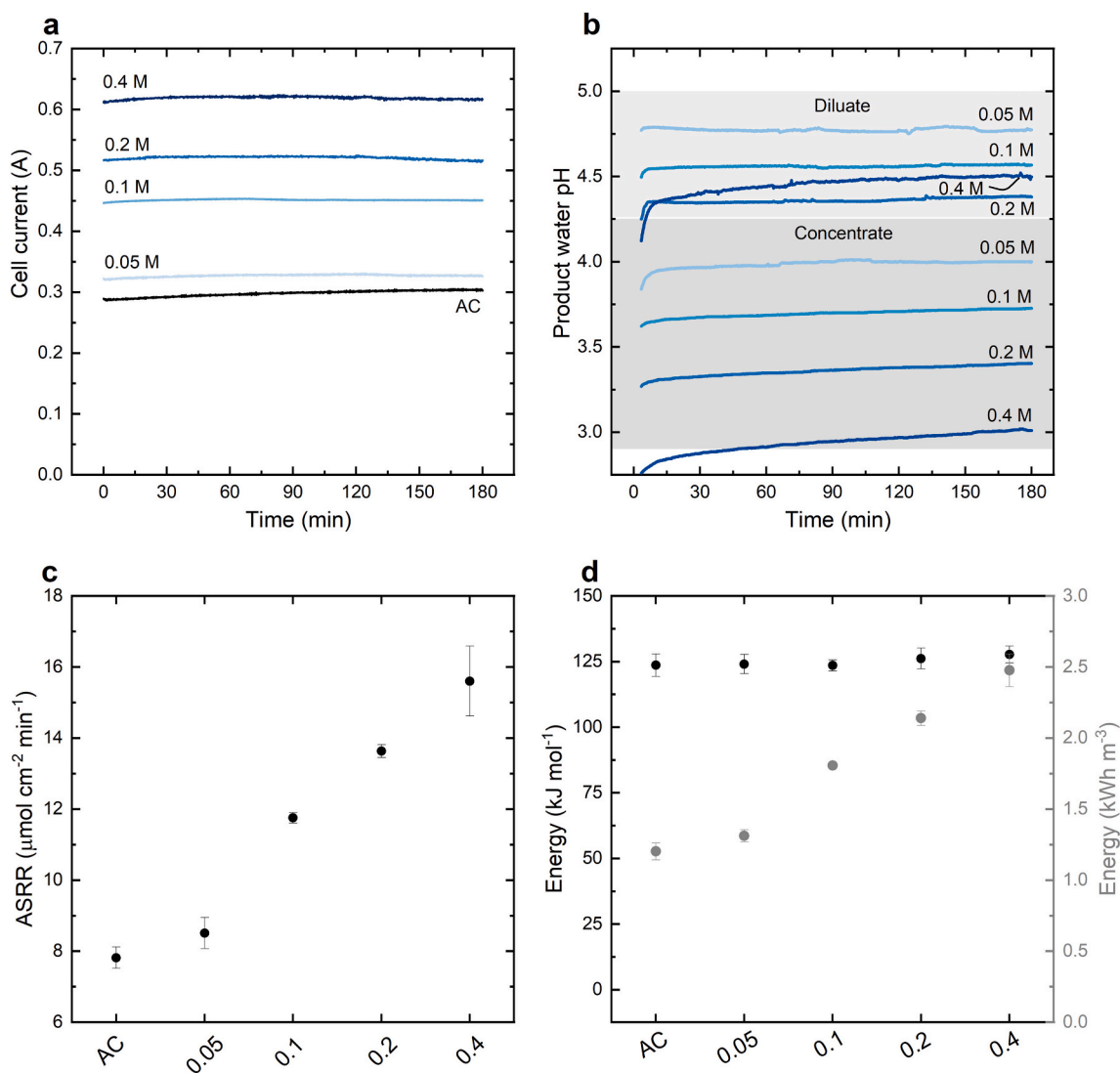


Fig. 2. Comparison of desalination performance with flow electrodes with several Fe – Cl concentrations and a typical FCDI AC slurry. (a) Comparison of the electrical current during desalination. (b) The pH of the water produced in diluate and concentrate channels. (c) The salt removal rate. (d) The energy consumption per mole of NaCl removed from the diluate and volumetric energy per volume treated in the diluate channel.

the activities as the ion concentration and the concentration change of the species in the current collector is negligible), the terms within the logarithm in both equations are equal and cancel each other. Consequently, the overall thermodynamical potential for the operation of the cell should be zero.

In this way, the potential drop in the cell mainly arises from three sources of resistance: the overpotentials of the Faradaic reactions; the resistance within the spacers (mainly in the diluate channel due to its lower salt concentration); the resistance of the membranes. In the case of cells with AC flow electrodes, the resistance in the spacers and membranes is equivalent to the Fe-Cl system. Consequently, the resistance of the flow electrodes is the main difference between the systems. The lower current for the AC flow electrodes suggests that the electron transfer resistance between the current collector and the AC particles is less favorable than in the Faradaic system.

Due to the lower resistance for electron transfer and the higher currents in the cell, the average salt removal rate (ASRR) also increases. As shown in Fig. 2c, the ASRR for the AC-only flow electrode, $7.8 \mu\text{mol cm}^{-2} \text{min}^{-1}$, is enhanced to $13.6 \mu\text{mol cm}^{-2} \text{min}^{-1}$ and $15.6 \mu\text{mol cm}^{-2} \text{min}^{-1}$, for the 0.2 M and 0.4 M of Fe-Cl. The energy

consumption per mol of NaCl is approximately 125 kJ mol^{-1} and remains stable for the AC-only and Fe-Cl flow electrodes. The energy consumption per volume of treated water leaving the diluate channel increases for the flow electrodes with Fe-Cl, as the electrical current in those experiments was higher. However, it should be considered that the experiments with higher current also have higher ASRR, thus resulting in a lower salt concentration in the diluate water. Suppose the experiments were run with a constant current. In that case, it would be expected that the system with Fe-Cl would result in lower cell voltages for higher Fe-Cl concentrations and, consequently, lower energy consumption per volume of treated water.

3.2. Comparison of desalination with AC + iron chloride vs. AC-only flow electrodes

Following the improved desalination rate achieved by Fe-Cl flow electrodes, the synergetic effect of the AC and Fe-Cl mixture was investigated. In Fig. 3, we compare the desalination performance across various flow electrode compositions. The cell current of the experiments with several Fe-Cl concentrations in the electrolyte is shown in Fig. 3a.

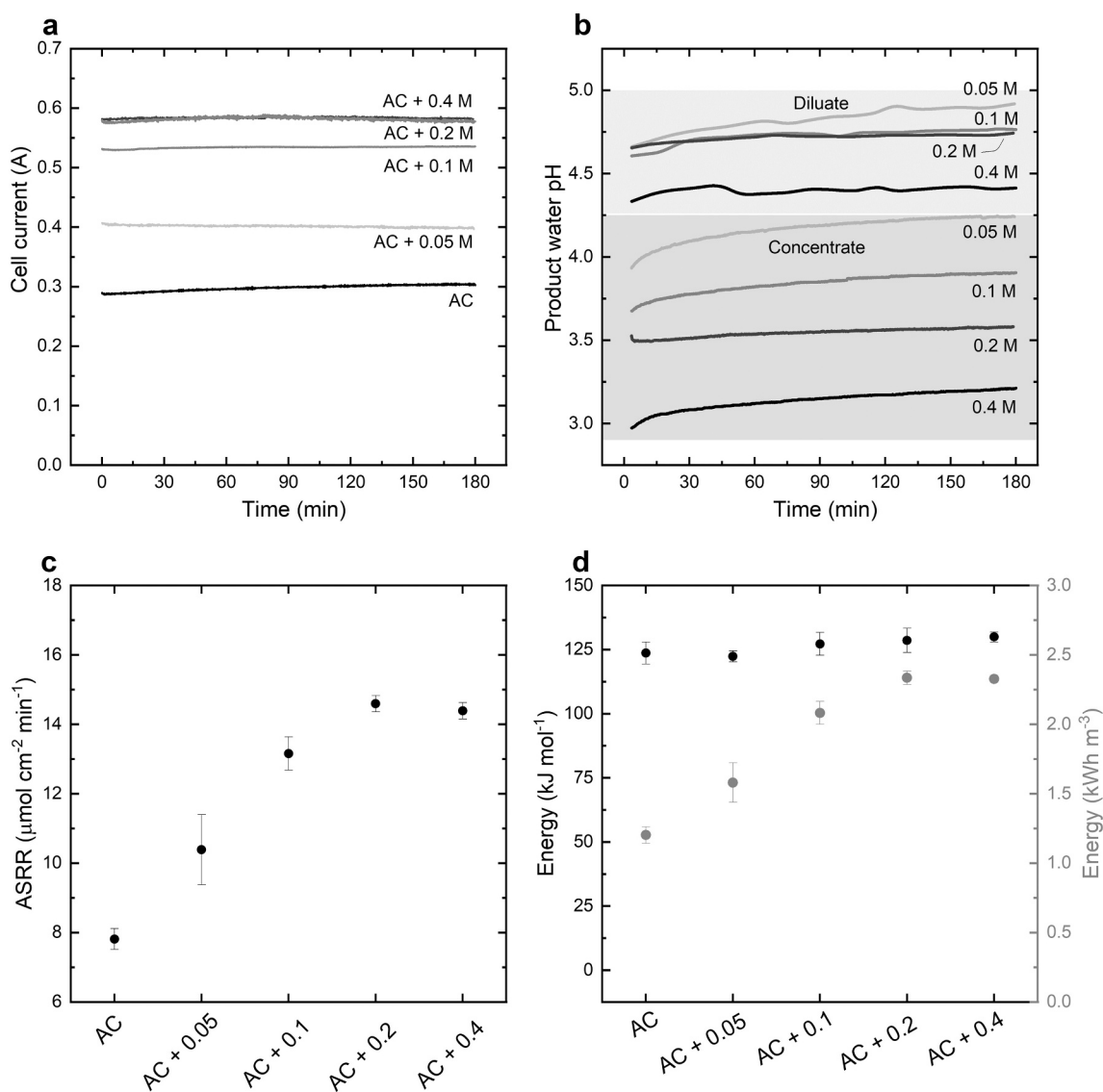


Fig. 3. Comparison of desalination performance with flow electrodes with AC and AC + different concentrations of Fe-Cl. (a) Comparison of the electrical current during desalination. (b) The pH of the water produced in diluate and concentrate channels. (c) The salt removal rate. (d) The energy consumption per mole of NaCl removed from the diluate and volumetric energy per volume treated in the diluate channel.

In Fig. 3a, it is shown that the mixed flow electrodes result in higher currents compared to the AC-only slurry. The average currents were approximately 441, 537, 584, and 584 mA, which means that the currents are higher in the AC + Fe – Cl than the same Fe concentration in the Fe – Cl system (except for 0.4 M of Fe_T). Furthermore, the increase in current becomes smaller as the iron concentration increases. For instance, increasing the iron concentration from 0.05 M to 0.1 M increased the cell current by around 96 mA, while increasing the concentration from 0.1 to 0.2 M increased the current only by 47 mA. For the conditions of the experiments investigated, increasing the Fe – Cl to 0.4 M in the presence of AC had no benefit. The smaller increment in current occurs due to a few factors. First, as the salt removal increases with the increase in Fe–Cl concentration, the diluate channel has 0.75 g L^{-1} of NaCl for the 0.2 M, while it has around 2.75 g L^{-1} of NaCl concentration in the experiment with 0.05 M. Thus, the resistance in the diluate channel is higher for 0.2 M. Second, the higher iron concentration in the flow electrode poses resistance to removing ions from the diluate channel. Finally, the iron concentration can affect the electrochemical kinetics of the Fe – Cl redox reaction, and the exchange current density and mass transfer of Fe – Cl species can change. However, this electrochemical investigation is out of the scope of this study.

The increase in current consequently increased the ASRR of AC + Fe – Cl flow electrodes, as shown in Fig. 3c. The highest ASRR value was obtained for the AC + 0.2 M Fe – Cl flow electrode, reaching $14.6 \mu\text{mol cm}^{-2} \text{ min}^{-1}$. This value is around 7 % higher than the flow electrode with the same Fe_T concentration and no AC, which had an ASRR of $13.6 \mu\text{mol cm}^{-2} \text{ min}^{-1}$. Although the AC + 0.4 M resulted in the same current, a slight decrease in the ASRR was observed – $14.4 \mu\text{mol cm}^{-2} \text{ min}^{-1}$ – which is slightly lower than the AC + 0.2 M experiments. A slight decrease in the current efficiency is the reason for this reduction, as the flow electrode compartment has more salt than the diluate and concentrate channels, and back diffusion can occur.

The energy consumption per mol was approximately the same for all experiments, around 125 kJ mol^{-1} . A slight increase can be observed in higher iron concentrations (Fig. 2d), as observed in the Fe – Cl flow electrodes. As previously discussed, the salt concentration of the water product is different. Hence, comparing the volumetric energy of different flow electrodes is not reasonable. For the highest desalination rate with AC + 0.2 M, the volumetric energy was 2.4 kWh m^{-3} , for a productivity of $134 \text{ L h}^{-1} \text{ m}^{-2}$ and a change in concentration in the diluate channel from 5 g L^{-1} to around 0.75 g L^{-1} .

The parameters investigated in this study show that the mixture of AC and Fe – Cl has a synergistic effect and improves the desalination compared to the typical FCDI flow electrode. This effect was previously observed in studies with Vanadium [4], Fe-CN [3], and organic redox couples such as TEMPO and Hydroquinone [3]. The experimental conditions of the present study and the other studies are very different regarding the salt concentrations, operational mode of the water channels (batch versus continuous), and the redox couple concentration. In this study, we investigate redox couple concentrations higher than the previous studies, as also done with Fe – CN only by Mohandass et al. [7] and Kim et al. [2]. In Luo et al. [3], for the flow electrode with 15 wt% of AC and 0.01 M of Fe-CN, the increase in the ASRR was around 25 %. We demonstrate here that increasing the concentration of Fe – Cl, up to 0.2 M affects the system positively, as the ASRR almost doubles.

It is important to note that the energy consumption associated with the operation of the pumps was not considered in the overall energy requirements for desalination. A trade-off assessment is necessary when considering the inclusion of AC in the system. On the one hand, the addition of AC offers advantages regarding the energy in the cell. On the other hand, the flow electrode with AC entails higher material costs and demands increased energy for the slurry pumping process. Addressing these concerns necessitates a dedicated study to comprehensively evaluate factors such as changes in viscosity, cost implications, and energy expenditure.

3.2.1. Analysis of water produced

The water product must meet specific salt concentration and pH criteria according to the application of water deionization, i.e., potable water production, ion recovery, or salt metathesis. For instance, for potable water production, the recommended pH should range between 6.5 and 8.5, according to the World Health Organization (WHO) [11]. The iron chloride species $\text{FeCl}_3/\text{FeCl}_2$ are both Lewis acids, as they can receive a pair of electrons. According to the Pourbaix diagram of the Fe – H_2O system and Fe – Cl – H_2O system (Fig. S1 and Fig. S2), there is a pH limit where the iron soluble species are stable without precipitating iron oxide, usually in the form of ferrihydrite [12]. This pH limit is increased by the presence of Cl^- as a ligand, but according to our preliminary experiments and other studies in the literature [13], at pH above 2.2, the Fe^{3+} precipitates. In this way, the pH of the flow electrode with Fe – Cl was not increased in our experiments, and the flow electrode had an acidic pH of approximately 1.7. As the concentration of ions is higher in the flow electrode than in the diluate and concentrate channels, it is necessary to measure the product water's pH and determine whether the iron species are crossing the membranes.

The pH of the flow electrode with AC-only results in the diluate channel water of approximately pH 10 and the concentrate channel pH of around 7, as shown in Fig. S3. Fig. 2b and Fig. 3b show the pH of diluate and concentrate channels for the experiments with Fe – Cl and AC + Fe – Cl, respectively.

For all the experiments, it is clear from Fig. 2b and Fig. 3b that the concentrate stream always has lower pH than the diluate. In the concentrate, a trend can be observed where the higher the iron concentration in the flow electrode, the lower the pH of the product water. Hence, it is likely that H^+ ions cross the membrane to the water channels, due to the low pH in the flow electrode. After 180 min, the pH of the concentrate in the experiments with Fe – Cl flow electrode was around 4.0, 3.75, 3.4, and 3.0, for the concentration of 0.05, 0.1, 0.2, and 0.4 M of Fe, respectively. For the same concentration of Fe_T on AC + Fe – Cl system, the pH of concentrate channels after 180 min was 4.5, 3.8, 3.6, and 3.24. Thus, it can be concluded that the presence of AC in the flow electrode slightly attenuates the change in pH in the concentrate channel. This effect could be due to the adsorption of iron chloride species onto the AC particles, slightly reducing the iron chloride concentration in the bulk solution. Also, as shown in Fig. S3, the pH of the concentrate channel in AC-only flow electrodes tends to be circumneutral and can also influence the concentrate pH.

Regarding the diluate channel, in the experiments with Fe – Cl-only (except for 0.4 M), there is also a trend where the higher iron concentration results in lower pH in the diluate channel, as shown in Fig. 2b. For the experiments with AC + Fe – Cl (Fig. 3b), the pH for the Fe_T concentration of 0.1 and 0.2 M are similar but lower than the pH for 0.05 M. Furthermore, the flow electrode with 0.4 M of iron has the lowest pH. Apart from some deviation, those results show a relevant influence of the iron concentration of the flow electrode on the water product pH. In a study using Fe – CN as a flow electrode, the reported pH of the diluate channel ranged from 6 to 8 [14]. Other studies with $\text{V}_2^+/\text{V}_3^+$ [4] and iron malonate [8] did not report the pH of flow electrodes and water streams. Vanadium salts result in a low pH electrolyte, and iron malonate was reported to have acid pH [13]. Here, our results suggest that the pH should continually be monitored when working with redox couples as additives for FCDI slurries or in electrolytes for RFD.

Besides the pH, it is also relevant to determine whether the redox couple contaminates the water. Samples of the product water in both diluate and concentrate channels were analyzed by ICP-OES to determine the Fe content. The results of the chemical analysis are present in Table 2.

As shown in Table 2, for the experiments with Fe_T of 0.05 M, the iron concentration in the product water is below the detection limit of the equipment for the experiments with AC + Fe – Cl. A low iron concentration of 0.02 mg L^{-1} ($0.36 \mu\text{mol L}^{-1}$) was found in the concentrate

Table 2

Iron concentration in $\mu\text{mol L}^{-1}$ and mg L^{-1} in the diluate and concentrate streams for different flow electrode compositions. The detection limit of iron is 0.01 mg L^{-1} .

Flow electrode	Iron concentration			
	[Fe]			
	molL^{-1}	Dil.	Conc.	
		μmolL^{-1}	mgL^{-1}	
0.05	–	0.36	<0.01	0.020
0.1	0.25	0.34	0.014	0.019
0.2	0.41	0.65	0.023	0.036
0.4	4.13	5.56	0.231	0.311
AC + 0.05	–	–	<0.01	<0.01
AC + 0.1	0.47	0.58	0.026	0.032
AC + 0.2	0.72	1.11	0.040	0.062
AC + 0.4	4.86	6.50	0.272	0.363

with no AC in the slurry. Iron was consistently detected in the water streams for the experiments with higher than 0.05 M Fe – Cl in the flow electrode. The Fe content in the product water appears to depend on the Fe concentrations in the flow electrode, as the iron concentration in the water increased with the concentration of Fe – Cl in the flow electrode. The iron concentration in the water stream increases relatively slowly for the flow electrodes up to 0.2 M of Fe_T. At 0.4 M, the iron concentration sharply increases in the water streams. Previously, studies did not observe the redox couple contamination [3,4], but the highest additive concentration investigated was below 0.05 M, which is the lowest concentration studied here. For another study with flow electrodes with 0.4 M of Fe – CN in an RFD cell, iron was found in the water stream in concentrations of $23 \mu\text{mol L}^{-1}$ in the concentrate and $0.7 \mu\text{mol L}^{-1}$ in the diluate.

As the salt concentration in the flow electrode is higher than in the water channels, especially the iron concentration, the ions migrate through the membranes to balance the concentration. It is also evident that the concentrate channel has a higher iron concentration than the diluate channels. The reason for the higher concentration in the concentrate can be the flux of ions. For instance, Cl^- ions cross the AEM from the cathode flow electrode to the concentrate channel. On the other hand, in the diluate channel, the Cl^- ions cross the AEM from the diluate to the anode compartment. The ion exchange membranes are not 100 % selective [15], and consequently, co-ions can cross the membranes. Thus, it is likely that some Fe – Cl species, despite their positive charge, cross the AEM along with the Cl^- to the concentrate stream.

As iron crosses the flow electrode and goes to the water channels, it is expected that the flow electrodes will be depleted in iron after some time. The time needed to decrease the initial iron concentration to 90 % ($t_{0.9}$) and 50 % ($t_{0.5}$) is estimated for 100 mL of electrolyte in the flow electrode used in the experiments. The iron loss in the experiments is assumed to remain constant, and no Fe – Cl was adsorbed in the AC. Table 3 presents the time for $t_{0.9}$ and $t_{0.5}$ in days.

For the flow electrode with AC + 0.05 M no iron was detected (Table 2). According to Table 3, the flow electrodes with concentrations of up to 0.2 M have a $t_{0.9}$ of at least 133 days. The flow electrodes with 0.4 M have fewer days until they lose 10 % of iron despite their higher concentration. As shown in Table 2, the iron loss rate was much higher for 0.4 M than for the other concentrations. Due to the lower iron

Table 3

Calculated iron loss based on the iron concentration of diluate and concentrated streams and the feed water flow rate.

Time (day)	Flow electrode							
	0.05	0.1	0.2	0.4	AC + 0.05	AC + 0.1	AC + 0.2	AC + 0.4
$t_{0.9}$	194	234	262	57	–	133	152	49
$t_{0.5}$	970	1172	1312	287	–	663	760	245

crossover, the flow electrodes with 0.05 and 0.1 M last longer until losing 10 % of their initial concentration. It is relevant to mention that those numbers may change in other experimental conditions. For instance, if the NaCl concentration is increased in the feed water, the diffusion of Fe – Cl species to the water channels may be lowered. However, based on the results presented here, it seems reasonable to assume that iron loss is not the major concern regarding the life-span of the flow electrode. FCDI and similar technologies are mostly on a lab scale, with a few reported scale-up studies. Thus, the minimum requirement for how long a flow electrode should last to be economically feasible (which also depends on its composition) is yet to be determined. Apart from the iron loss, we also foresee that water crossover (due to osmotic effects) from the feed stream to the flow electrode may play an important role in the process. Nonetheless, we could not observe water cross for those sets of experiments lasting 180 min, and more extended duration tests (e.g., a few days) should be performed in the future.

3.3. Desalination with Fe – Cit

As demonstrated by our previous results, the acid flow electrode changes the pH of the water channels. Hence, we investigate how to increase the pH of the flow electrodes with Fe – Cl to control the pH of flow channels. However, the solubility of the Fe^{3+} in the Fe – Cl system is restricted by around pH 2.2, according to our experiments. As previously shown in redox flow batteries, the pH of iron-based organic complexes electrolytes can be increased to a greater extent while avoiding precipitation [13]. Hence, citrate was chosen as a complexant, as iron citrate and citrate are not hazardous in low concentrations in water. Also, citrate is used as an additive in several foods, does not pose a risk to human health, and is not an expensive chemical, keeping the objective to use a non-expensive additive in FCDI flow electrodes.

The highest desalination rate with a Fe – Cl system without iron contamination, superior to the WHO standards, was obtained with 0.2 M of Fe_T in the flow electrode. Thus, the same concentration of Fe_T was tested in the desalination experiments, and the flow-electrode electrolyte consisted of iron and citrate in the concentration of 0.2 M and 0.6 M, respectively. The experiments were run with and without AC, and the pH of the flow electrode was 5.41, with no pH adjustment prior to the tests. The membrane configuration of the cell was changed compared to the Fe – Cl based flow electrode. The expected Fe – Cit complexes and the citrate ion are negatively charged [16]. Thus, two cation exchange membranes (adjacent to the flow electrodes) and one anion exchange membrane between the concentrate and diluate spacers were used. For the system with the Fe – Cit salt only, the reaction at the anode and cathode are represented, respectively, in Eq. 10 and Eq. 11.

Anodic reaction:



Cathodic reaction:



The desalination performance of Fe – Cit based flow electrodes is presented in Fig. 4. The cell current for 0.2 M of Fe – Cit and the 0.2 M of Fe – Cl are compared in Fig. 4A with and without AC.

It is shown in Fig. 4a that the current for the flow electrode with citrate was lower than the current with Fe – Cl. The current was around 54 % higher for the Fe – Cl system compared to Fe – Cit, without AC in the flow electrode. The Fe – Cit species are bigger than Fe – Cl ones, and the diffusion coefficient is lower for the Fe – Cit. The diffusion coefficient for 0.1 M of FeCl_3 was found to be $4.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, and $5.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for FeCl_2 [13]. For the same concentration, the Fe-Cit species (Fe^{III} species) have a lower diffusion coefficient, $1.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. Furthermore, the exchange current density (i_0) reported for Fe – Cl and Fe – Cit species on a glassy carbon working electrode are

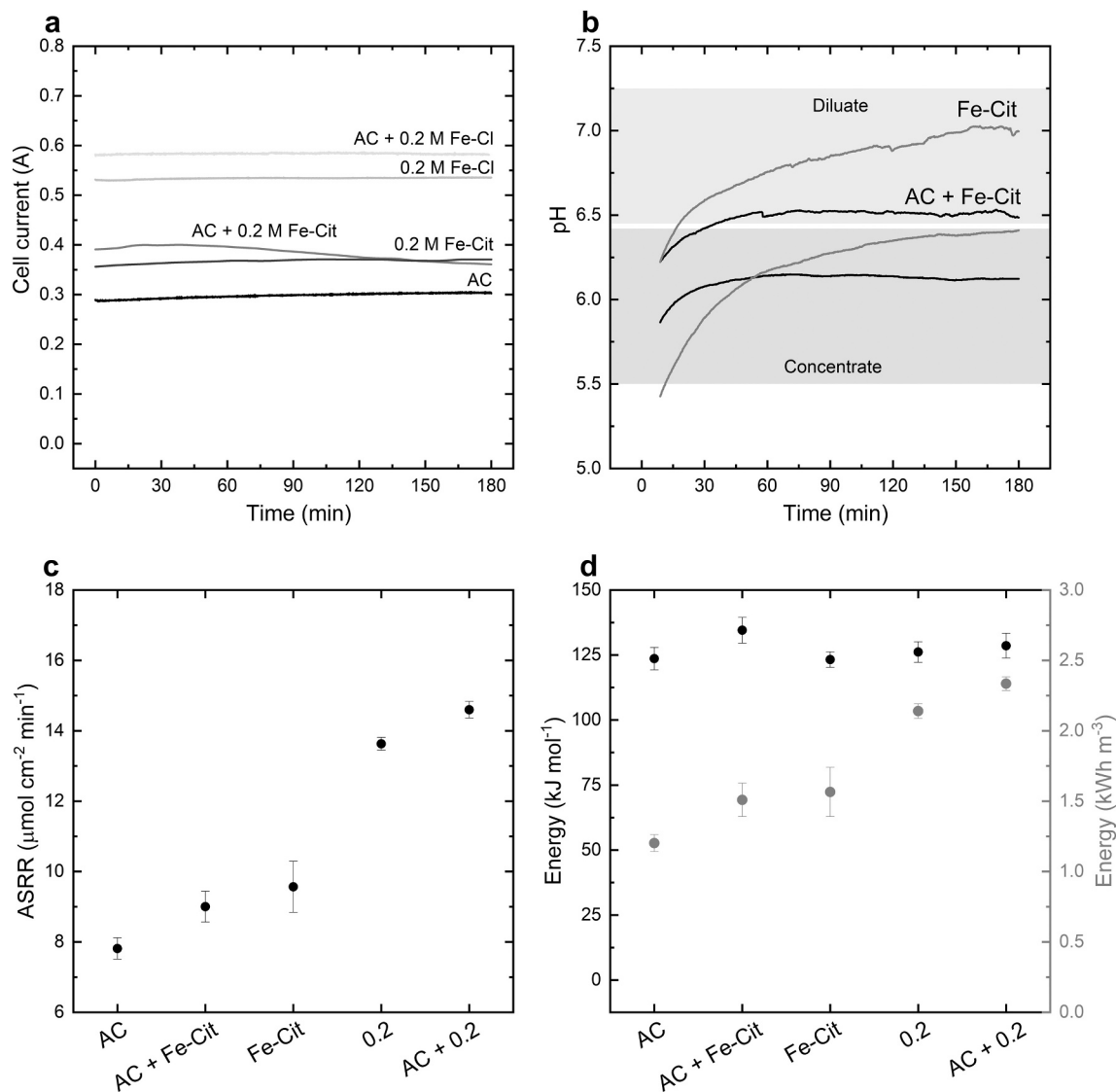


Fig. 4. Desalination performance of flow electrodes with AC and AC + Fe – Cit slurries. (a) The electrical current during desalination. (b) The pH of the water produced in diluate and concentrate channels. (c) The salt removal rate. (d) The energy consumption per mole of NaCl removed from the diluate and volumetric energy per volume treated in the diluate channel.

2.3 and 0.9 mA cm⁻² [13], respectively. As previously discussed for the Fe – Cl based flow electrodes, it is necessary to investigate the controlling step in the faradaic reactions of those Fe-based species in the future. In this study, as the flow rate of the flow electrode was 200 mL min⁻¹, and the concentration of iron species did not significantly change inside the current collector, the diffusion of species likely had a lower effect on the electrochemical kinetics here. Thus, the exchange current had a larger influence on the electrochemical kinetics.

The currents of AC + Fe – Cit and Fe – Cit flow electrodes after 180 min of the experiment were around 350 mA, which is more than the AC-only flow electrodes. For the AC + Fe – Cit, the current started around 400 mA but then decreased over time and remained close to the current of Fe – Cit system. After 120 min of the experiment, the presence of AC in the flow electrode had no advantage compared to Fe – Cit regarding the desalination current. However, comparing the ASRR of Fe – Cit flow electrode, 9.6 μmol cm⁻² min⁻¹, and the ASRR for AC + Fe – Cit, 9.0 μmol cm⁻² min⁻¹, it was shown that desalination rate was higher for Fe – Cit. Also, the energy per mol of salt removed was slightly higher for AC + Fe – Cit than Fe – Cit. Then, the mixture of AC and Fe – Cit does not seem to be an advantage, considering the desalination rate and the

energy consumption. AC + Fe – Cit consumed around 135 kJ mol⁻¹, while only Fe – Cit consumed 123 kJ mol⁻¹. The possible reason for no improvement in the desalination rate in the presence of AC in the Fe – Cit flow electrode is possibly due to the citrate or iron citrate adsorption. Previous studies have investigated AC flow electrodes with organic redox couples, such as sodium anthraquinone-2-sulfonate (AQS), 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), hydroquinone (HQ) [3]. Those organic species alone presented very similar desalination rates compared to their mixture with AC. Those organic compounds were found to have a strong affinity for the AC surface. The adsorption of species onto the surface of the AC reduces the concentration of the redox couples in the electrolyte, and it can increase the energy necessary to charge the electron transfer from the current collector to the AC.

3.3.1. Analysis of water produced by the Fe – Cit based flow electrodes

The pH of the diluate and concentrate channels are shown in Fig. 4b. In both flow electrodes with Fe – Cit, the pH was increased relative to the Fe – Cl based flow electrodes. In the presence of AC, however, the increase was slightly smaller, and after 180 min of the experiments, the diluate and concentrate had approximately pH 6.5 and 6.1, respectively.

On the other hand, the diluate and concentrate streams with no AC had pH 7 and 6.4, respectively. In another study with Fe – Cit and a redox flow battery setup [7], the pH of the flow electrode was adjusted to 7. However, the pH of the diluate and concentrate channels was not reported. Here, the higher pH of the Fe – Cit system relative to the Fe – Cl is due to the natural pH of the flow electrode, which is around 1.7 in Fe – Cl and 5.4 in the Fe – Cit system. Hence, it is relevant to control the pH of the flow electrode and find soluble redox couples in circumneutral pH if the intended application is the production of potable water or a low pH of the product water is undesirable.

Concerning the crossover of ions in the citrate system, in this case, not only is the iron relevant, but also the citrate is of interest. The citrate anions were in stoichiometric excess compared to the iron, so some free citrate could cross the membrane. Iron citrate is expected to be found in anionic form at the experimental conditions, and the iron citrate is larger than iron chloride, so a lower crossover of iron crossover was expected. The concentration of iron and Total Organic Carbon (TOC) are shown in Table 4.

Table 4 shows that for both flow electrodes based on Fe – Cit, the iron concentration in the water streams was below the detection limit of the equipment. That indicates that for the same concentration Fe – Cl (0.2 M), there is less iron crossing the membrane in the citrate system. The reason is the size of the iron citrate species, which has two citrate ions coordinated with an iron center. In the literature, it was reported iron contamination of 0.7 and 0.2 $\mu\text{mol L}^{-1}$, for a 0.4 M of Fe_T and 1.2 M of citrate [7]. Regarding the citrate, the TOC analysis indicated the presence of organic carbon in the water. The crossover was lower for the flow electrode with AC, as likely AC adsorbs some citrate. As iron was not found in the water channels, it is reasonable to assume that free citrate ions that are not bonded to the iron are permeating the membrane. Again, the concentrate water stream shows a higher concentration of crossover ions than the diluate, which aligns with the results shown elsewhere [7]. However, in the present study, the highest contamination in the concentrate channel was 0.494 mg L^{-1} (equivalent to 2.61 $\mu\text{mol L}^{-1}$ of citrate), while 2.56 mg L^{-1} (36 $\mu\text{mol L}^{-1}$ of citrate) was found in the study of Mohandass et al. [7]. However, this study has a flow electrode 0.4 M of Fe_T and 1.2 M of citrate. Considering the experimental conditions of this work, the iron citrate complex is an interesting alternative to AC slurries regarding the desalination rate. However, the loss of citrate ions must be considered, and likely, over long-run experiments, the flow electrode composition must be monitored and controlled.

3.4. Analysis of desalination performance

The review of Wang et al. [17], and the work of Kim et al. [18] and, Mohandass et al. [7], presented the desalination performance of flow electrodes with different compositions. The comparison of desalination performance of different studies is often complicated as several operational parameters influence the energy consumption and salt removal rate. For instance, several previous studies investigated the desalination of FCDI and RFD with the feed water in a batch mode, while here, we used a single-pass setup. Furthermore, the salt concentration of the feed water and the variation in concentration between the initial and final salt concentration affect the productivity (volume of water produced per

area of membrane and time) and salt removal rates.

The productivity of water production reported in several studies ranges from 0.5 to 164 $\text{L h}^{-1} \text{ m}^{-2}$ [7]. From a perspective of application, we considered that desalination results of FCDI or RFD are more realistic when 1.2 V are applied or current densities that result in cell voltages closer to 1.2 V. Operating with low current densities and low voltages results in lower energy consumption. For instance, a previous study obtained low energy consumption (62 kJ mol^{-1}) with redox couples and carbon nanotubes but at very low productivity [4], of approximately 3 $\text{L h}^{-1} \text{ m}^{-2}$. However, it would be necessary to higher membrane areas (higher capital cost) to obtain the same water production volume as other studies.

In this way, the results obtained for the flow electrodes with 0.4 M of Fe – Cl are compared to other studies with similar operational parameters. In this study, the flow electrode with 0.4 M resulted in the highest ASRR (15.6 $\mu\text{mol cm}^{-2} \text{ min}^{-1}$), for a productivity of 134 $\text{L h}^{-1} \text{ m}^{-2}$, energy consumption of 125 kJ mol^{-1} and a variation of salt concentration from the feed water 5 g L^{-1} (0.086 M) to around 0.59 g L^{-1} (0.01 M) in the diluate channel.

The results reported by Kim et al. [18], with 0.04 M of Fe – CN as a redox couple showed an ASRR of 1.53 $\mu\text{mol cm}^{-2} \text{ min}^{-1}$ for feed water of 0.1 M of NaCl, and energy consumption of 124 kJ mol^{-1} . The energy consumption is similar to the results obtained in this study, and the ASRR is lower. However, the salt solution was operated in a batch mode, and the redox couple concentration was lower than in our study.

In Mohandass et al., [7] Fe – Cit was used as a redox couple (0.4 M) in the flow electrode. The feed water consisted of 0.05 M of NaCl, and the diluate concentration was 0.0086 M, for a productivity of 41.1 $\text{L h}^{-1} \text{ m}^{-2}$. The energy consumption was 0.48 kWh m^{-3} . Here, we obtained a higher productivity (134 $\text{L h}^{-1} \text{ m}^{-2}$) and a higher desalination rate. This is mainly due to the better desalination performance of Fe – Cl over Fe – Cit, as shown in this study, and the higher salt concentration (5 g L^{-1}) in the feed water evaluated here.

Xie et al. [6] investigated 0.1 M of Fe – DTPA as a redox couple and a saline feedwater with 0.05 M of NaCl. For 1.0 V applied on the cell, an ASRR of 2.5 $\mu\text{mol cm}^{-2} \text{ min}^{-1}$ and energy consumption of 554 kJ mol^{-1} was achieved. The study of [3] investigated several redox couples along with AC for feed water consisting of 2 g L^{-1} of NaCl. The best desalination rate was achieved by mixing 0.01 M of Fe – CN with 15 wt% of AC. The ASRR was found to be 0.94 $\mu\text{mol cm}^{-2} \text{ min}^{-1}$, and productivity of 64.1 $\text{L h}^{-1} \text{ m}^{-2}$.

In summary, the results of the Fe – Cl system show higher ASRR than previous studies and high productivity. It indicates that Fe – Cl is an attractive redox couple for desalination and that higher concentrations (0.2 to 0.4 M) of redox couple provide much better salt removals than the lower concentration used in some studies (lower than 0.1 M). Furthermore, reasonable energy consumption can be achieved even at high desalination rates. Due to the low pH of Fe – Cl flow electrodes and iron crossover, new strategies to overcome those issues are necessary or other redox couples in future studies.

4. Conclusion

This work investigated a typical FCDI cell's desalination performance by introducing iron-based additives: iron chloride and iron citrate. The system was compared with flow electrodes with typical activated carbon, only the redox couples, and the mixture of activated carbon and redox couples additives.

It was demonstrated that both Fe – Cl and Fe – Cit – activated carbon-based flow electrodes enhance the desalination performance compared to a 15 wt% AC flow electrode. In the Fe – Cl system, even the lowest concentration of 0.05 M shows higher cell current and increased salt removal rate by 10 % compared to activated carbon only. The Fe – Cl was shown to increase the desalination rate up to a concentration of

Table 4

Iron and total organic carbon concentration in the diluate and concentrate channels for flow electrode based on Fe-Cit electrolyte.

Flow electrode	Iron concentration		Total Organic Carbon	
	Diluate	Conc.	Diluate	Conc.
	mg L^{-1}		mg L^{-1}	
Fe-Cit	<0.01	<0.01	0.474	0.494
AC + Fe-Cit	<0.01	<0.01	0.269	0.349

0.4 M, reaching a salt removal rate of $15.6 \mu\text{mol cm}^{-2} \text{min}^{-1}$, compared to $7.8 \mu\text{mol cm}^{-2} \text{min}^{-1}$ for the flow electrode with only AC. This represents a 100 % increase in the desalination rate. In the flow electrode based on activated and Fe – Cl, 0.2 M has the highest salt removal rate of $13.6 \mu\text{mol cm}^{-2} \text{min}^{-1}$, which is an increase of 74 % compared to AC slurry.

The Fe – Cl was found to reduce the pH of the product water, and the higher the concentration, the lower the pH. The concentrate channel has lower pH than the diluate channel, ranging from 4.25 to 3.25. Furthermore, iron was found to cross the membranes, and the contamination became more relevant at 0.4 M of Fe – Cl. The optimum iron concentration for the iron chloride was 0.2 M, where the desalination rate was high, and the iron levels were still low in the water channels.

The iron citrate was compared to the iron chloride at 0.2 M of Fe_T . It was demonstrated that the citrate-based flow electrodes perform better than the AC-only flow electrode. The salt removal rate for the citrate system is lower than Fe – Cl. However, the product water's pH is circumneutral, making this system a better option for potable water consumption. No iron was detected in the water streams, and citrate ions were found in the product water ranging from 1.4 to $2.6 \mu\text{mol L}^{-1}$. Finally, the mixture of iron citrate with the AC does not seem to benefit the desalination current and salt removal rate.

Based on our results, it is shown that iron-based redox couples present an interesting low-cost alternative for additives for FCDI flow electrodes. The appropriate additive and its concentration should be chosen considering the application of ion removal. In future research, other additives that reduce the cross-over of the iron and the complexant but still have good electrochemical kinetics are of interest.

CRediT authorship contribution statement

Nelson H.J. Freire: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Christian J. Linnartz:** Conceptualization, Investigation, Methodology, Project administration, Resources, Writing – original draft, Writing – review & editing. **Luciano Montoro:** Conceptualization, Writing – original draft, Writing – review & editing. **Virginia S.T. Ciminelli:** Supervision, Writing – original draft, Writing – review & editing. **Matthias Wessling:** Funding acquisition, Resources, Supervision, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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