



## Redox-active coordination polymers as bifunctional electrolytes in slurry-based aqueous batteries at neutral pH



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### ABSTRACT

Highly water-dispersible, redox-active 1D coordination polymers (CPs) have been synthesized using low-cost precursors. These CPs, containing chloranilic acid as organic ligand and a transition element, such as Fe and Mn as a metal center, form long-term stable slurries containing up to 100 g/L solid particles in aqueous media (0.5 M NaCl, 1 mg carbon nanotubes). Voltammetry studies showed that the iron-based particulate slurries exhibited three different redox stages with no metal plating. However, the suspensions with manganese-based coordination polymers experienced a metal plating process in the same potential window range as for the iron-based CPs. Moreover, the particulate suspension of iron-CPs shown longer-term stability than their isostructural analogs based on manganese. The 1D Fe-CPs were used as catholyte and anolyte in a symmetrical cell with a low-cost size exclusion cellulose membrane acting as a separator. The cell experienced a reversible capacity value of 45 mAh/g (225 mAh/L) at a current density value of 20 mA/g for 50 cycles (~12 days) at neutral pH. This study opens the possibility of using inexpensive coordination polymers as single bifunctional electrolyte material in aqueous batteries and other sustainable energy storage-related systems.

### 1. Introduction

The contribution of renewable sources such as wind and solar for energy production is expected to increase from 4% nowadays to 25% in the year 2030 [1]. These renewable sources are however intermittent, so it is necessary to complement them with energy storage devices. Although the cost of the principal energy storage systems has significantly decreased over the last years, it still is one of the main obstacles for large-scale renewable energy implementation [2].

Redox-flow batteries (RFBs) are one of the prominent electrochemical energy storage devices to be coupled with renewable energy sources due to their flexible design, power/energy decoupling, and scalability [1]. However, the high cost of some of their components such as vanadium acidic electrolytes and Nafion membranes is hampering their widespread application [3]. In addition, the inefficiency of the membranes causes capacity losses over time and limits the lifetime of the batteries [4,5].

Considering these drawbacks, the development of earth-abundant based and environmentally friendly active materials together with

the progress in new strategies to avoid the use of ion-exchange membranes have attracted growing interest [6]. One of the alternatives pursued is the replacement of Nafion membranes with low-cost porous separators. However, to put this into practice, it is necessary to increase the size of the redox materials to minimize crossover. On the other hand, redox active materials based on earth abundant elements that can be incorporated in neutral aqueous electrolytes are being studied as a way to reduce the cost and increase safety. In this respect, the development of electroactive polymers offers a wide range of possibilities. Nevertheless, the polymers solubility in water is an important limitation and to overcome it, the formulation of electrolytes based on dispersions and slurries is being intensively studied [7]. Poor solubility of species has led to the creation of hybrid RFBs, where the system comprise at least one solid electroactive material that is deposited within the stack. As drawback, these hybrid batteries differ from the common RFBs in their capability to decouple power and energy, which is limited by the solid electrode [8].

A recently developed redox-flow battery based on the acidic aqueous dispersion of micro-sized all-polymer redox-active particulates

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(1 mol L<sup>-1</sup>), has shown excellent electrochemical properties such as highly reversible multi-electron redox process, rapid electrochemical kinetics, and ultra-stable long-term cycling capability [9]. The application of these particulate slurries along with the use of electroactive polymer solutions [10] or colloids electrolytes [11] also makes it possible to replace expensive ion-conducting membranes with much cheaper, commercial dialysis membranes operating through the mechanism of size exclusion. Because the use of slurries enhances flexibility and portability, slurry-based batteries have also attracted attention that otherwise suffers from bulky construction. Slurries can also be as raw materials for printable batteries making assemblies faster and more economical [12]. A significant challenge to be overcome remains the dispersion and stabilization of redox-active materials without using surfactants or emulsifiers given that a large number of such materials are not water-soluble.

Coordination polymers (CPs) are comprised of metal centers connected to organic linkers that result in a wide variety of crystalline porous structures with a large range of applications as catalysts, gas adsorption substrates, and electrode materials in energy [13]. Their physical and chemical characteristics make CPs potential systems to devise water-based slurries functioning as a multiredox electrolyte in RFBs. The use of homogeneously dispersed CP particulates as electroactive materials will allow overcoming their solubility limit in aqueous media. Moreover, the application of CPs suspensions will make it possible to replace the expensive ion-exchange membrane currently used by low-cost dialysis membranes.

Herein, inspired by the chemical and structural properties of the coordination polymers synthesized by Kawata et al. [14] with the formula  $\{[M(\text{CA})(\text{H}_2\text{O})_2]_n\}$ , (M = Fe<sup>II</sup>, Mn<sup>II</sup>, and Co<sup>II</sup>) (CA = chloranilic acid, Fe and Mn isostructural polymer analogs exhibiting a particle size around 500–600 nm have been prepared. The reduced particles size has allowed to obtain of stable slurries of these 1D CP particulates with a content up to 100 g/L. We have also characterized their physico-chemical properties and studied their electrochemical properties in aqueous media at neutral pH value. The Mn polymer had two major non-reversible redox processes at -0.5 and 0.9 V vs SHE, while the Fe CP has shown two major reversible redox stages at -0.3 and 0.7 V vs SHE, having the possibility of serving indistinctively as the positive or negative electrolyte. This multi-redox activity drove us to test a cell where the iron-based slurries acted as a single redox component in the aqueous electrolyte in a symmetrical system, with low-cost cellulose membranes as exclusion separators.

## 2. Experimental

### 2.1. Materials

The precursors materials, chloranilic acid, iron sulphate nonahydrate (FeSO<sub>4</sub>·9H<sub>2</sub>O), and manganese sulphate tetrahydrate (MnSO<sub>4</sub>·4H<sub>2</sub>O) were supplied by Sigma-Aldrich, and used without further purification. The porous carbon felt with a thickness of 2.5 mm was from SIGRACELL® Battery Felts (GFD2.5EA). The wetted area of the carbon felt is around 360 cm<sup>2</sup>, according to the felt mass (0.06 g) and the BET surface area (0.6 m<sup>2</sup>/g). The cellulose membrane was a CelluSep T-series dialysis membrane with a pore size of 8 kDa and 1 kDa. Carbon nanotubes (CNT) of multi layer wall, with an 20 nm outer average diameter were used as a conductive additive.

### 2.2. Synthesis of the CPs

The room temperature synthesis (~25 °C) for each coordination polymer was the following:

$\{[\text{Fe}(\text{CA})(\text{H}_2\text{O})_2]_n\}$  (water). 83.5 mg of chloranilic acid (0.4 mmol) were dissolved in 60 mL of warm deionized water and then combined with a solution of 111 mg of FeSO<sub>4</sub>·9H<sub>2</sub>O (0.4 mmol) in

20 mL of warm deionized water. Immediately after mixing, dark crystals began to form. After one week crystals were filtered off, washed with water and dried in air. Yield: 93%.

$\{[\text{Mn}(\text{CA})(\text{H}_2\text{O})_2]_n\}$  (water). This hybrid complex was prepared following the same procedure than for  $\{[\text{Fe}(\text{CA})(\text{H}_2\text{O})_2]_n\}$  but with MnSO<sub>4</sub>·4H<sub>2</sub>O as a metal precursor. After one week, crystals were filtered off, washed with water and dried in air. Yield: 90%.

$\{[\text{Fe}(\text{CA})(\text{H}_2\text{O})_2]_n\}$  (methanol). 225 mg of chloranilic acid (1.08 mmol) were dissolved in 32 mL of methanol and then combined with a saturated solution of 300 mg of FeSO<sub>4</sub>·9H<sub>2</sub>O (1.08 mmol) in 2 mL of warm deionized water. Immediately after mixing, dark crystals began to form. After one hour the crystals were filtered off, washed with water and dried in air. Yield: 85% .

$\{[\text{Mn}(\text{CA})(\text{H}_2\text{O})_2]_n\}$  (methanol). This hybrid complex was prepared following the same procedure as the previous one, but with MnSO<sub>4</sub>·4H<sub>2</sub>O as a metal precursor. After one week the crystals were filtered off, washed with water and dried in air. Yield: 80%

The general reaction for the formation of the coordination polymers is shown as follows:

## 3. Characterization methods

The crystalline structure of the Fe and Mn 1D CPs was analysed by powder X-ray diffraction (XRD) in the 2θ range of 5°–60° by using a Bruker D8 Advance diffractometer with CuKα radiation (α = 1.54 Å). An FTIR Perkin Elmer UATR two was used to qualitatively analyse in the range of 4000 to 400 cm<sup>-1</sup> the functional groups of the coordination polymers. The morphology, shape, and size of the synthesized coordination polymers particles were studied by high resolution scanning electron microscopy (HRSEM) in a Hitachi S-8000 model with field emission filament and a voltage of 1.0 kV.

Permeability tests were carried out in an U-shaped cell. An aqueous suspension with a concentration value of 1 g/L of the coordination polymer  $\{[\text{Fe}(\text{CA})(\text{H}_2\text{O})_2]_n\}$  was introduced in one branch of the U-cell and in the other side of the U-cell only deionized water was placed. A dialysis cellulose membrane as a separator was mounted in the middle of the cell avoiding the mixing of the two suspensions. Two membranes with different pore size, 1 kDa (0.88 nm) and 8 kDa (1.75 nm), were used. After 20 days the water solution was tested by UV-vis with a Lambda 35 Perkin Elmer spectrophotometer.

The electrochemistry of the CPs was studied in a VMP3 multichannel potentiostat/galvanostat (Bio-Logic). The study of the influence of the pH in the electrochemical properties of the CPs was accomplished by cyclic voltammetry using a three-electrode configuration with a porous carbon felt material acting as working electrode (wetted area is around 360 cm<sup>2</sup>), an Ag/AgCl electrode as the reference electrode and a platinum wire as a counter electrode in a potential range between -1.5 V and 1.5 V vs. Ag/AgCl, at different scan rates. The porous carbon felt was activated at 400 °C for 12 h to increase its hydrophilicity and then its wettability with the electrolyte. The potential values have been converted into the values corresponding to the standard hydrogen electrode (SHE) scale for a clear comparison with those redox potential values corresponding to each metal pair, which are calculated in such scale. The slurry contained 100 mg of the polymeric material and 1 mL of a 0.5 M aqueous NaCl and 1 mg of carbon nanotubes (CNT) so that the final polymer/CNT mass ratio was 100/1. The pH value of the slurries was adjusted to 9 or 5 by using either 1·10<sup>-5</sup> M NaOH or 1·10<sup>-5</sup> M HCl.

The battery concept was demonstrated in a 6 cm × 8 cm Plexiglas symmetric cell by applying galvanostatic charge-discharge cycles under a voltage range between 0 V and 0.9 V. The 2.5 mm thick porous carbon felt (electrode) was activated at 400 °C during 24 h. A dialysis membrane with a pore size of 1 kDa acted as separator. The protocol for measuring the electrochemical properties of the battery was the following: 50 mg of the iron-based CP  $\{[\text{Fe}(\text{CA})(\text{H}_2\text{O})_2]_n\}$  was

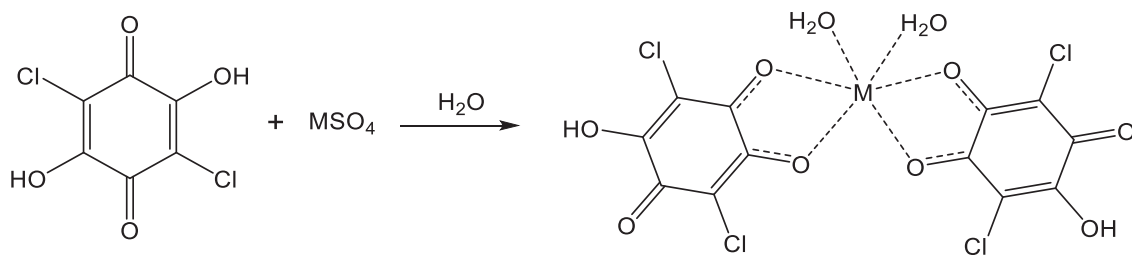


Fig. 1. General reaction of the formation of the coordination polymers  $\{[M(CA)(H_2O)_2]H_2O\}_n$ .

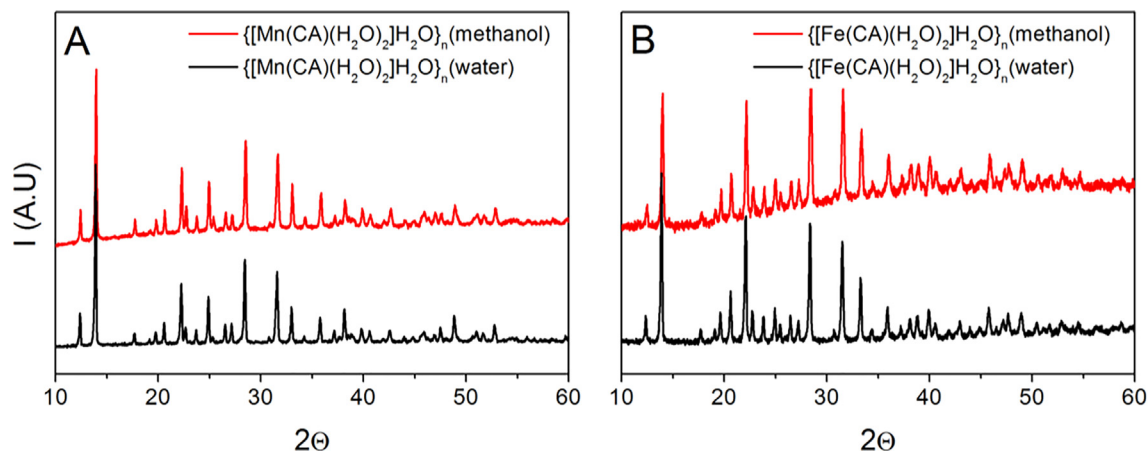


Fig. 2. Powder X-ray diffraction pattern of the CPs  $\{[Mn(CA)(H_2O)_2]H_2O\}_n$  (A) and  $\{[Fe(CA)(H_2O)_2]H_2O\}_n$  (B) synthesized either in water or methanol.

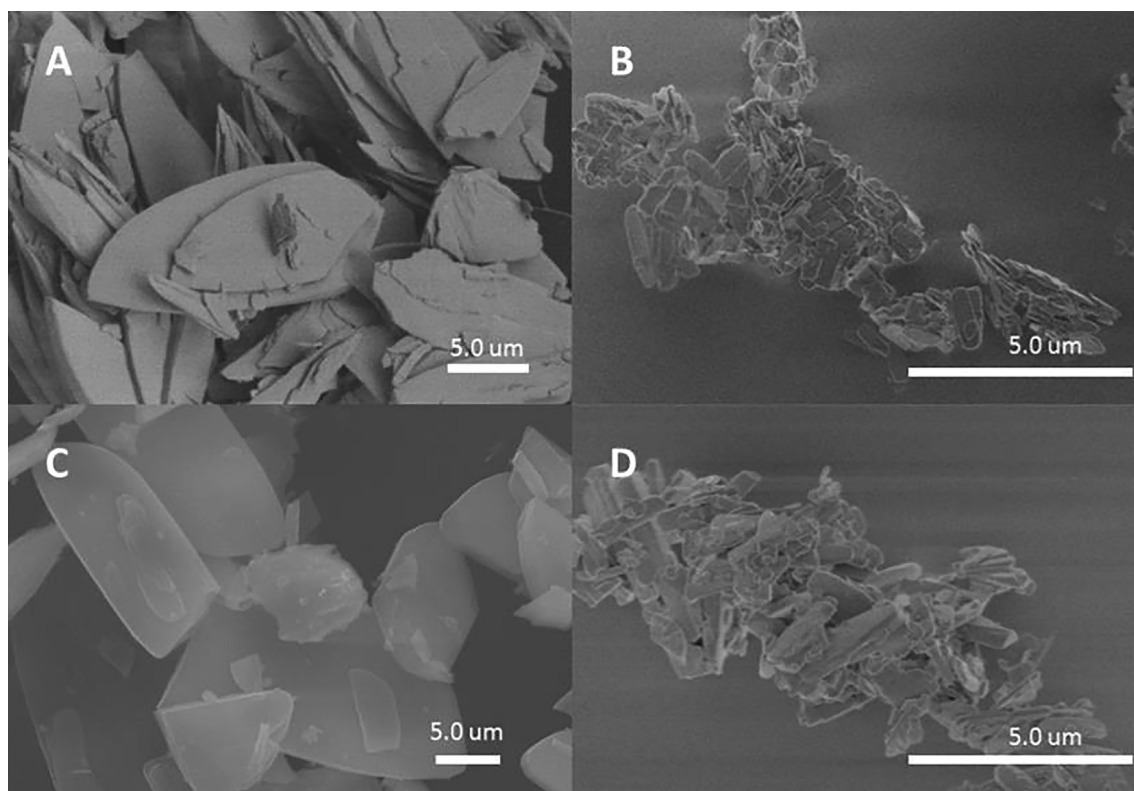
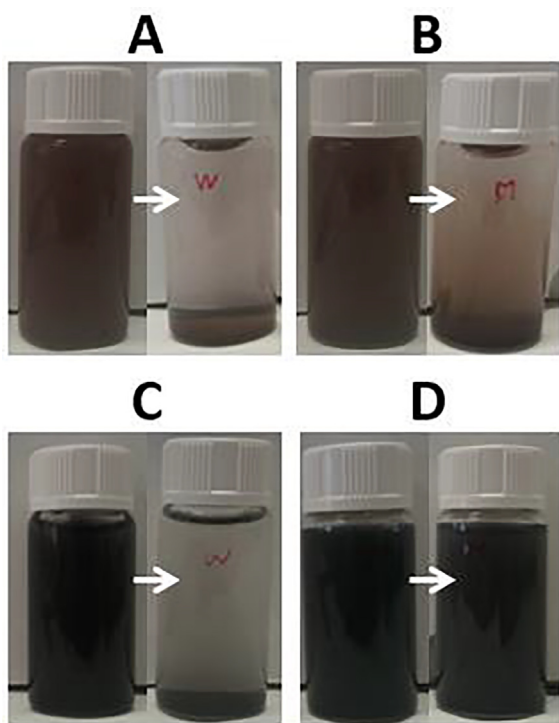


Fig. 3. SEM images of the 1D CPs isostructural analogues synthesized in water (A and C) or methanol (B and D):  $\{[Mn(CA)(H_2O)_2]H_2O\}_n$  (A)-(B) and  $\{[Fe(CA)(H_2O)_2]H_2O\}_n$  (C)-(D).



**Fig. 4.** Stability test for the polymer particulates aqueous suspensions with a concentration of 1 g/L after 72 h: {[Mn(CA)(H<sub>2</sub>O)<sub>2</sub>]H<sub>2</sub>O}<sub>n</sub> synthesized in water (A) and methanol (B) and {[Fe(CA)(H<sub>2</sub>O)<sub>2</sub>]H<sub>2</sub>O}<sub>n</sub> synthesized in water (C) and methanol (D).

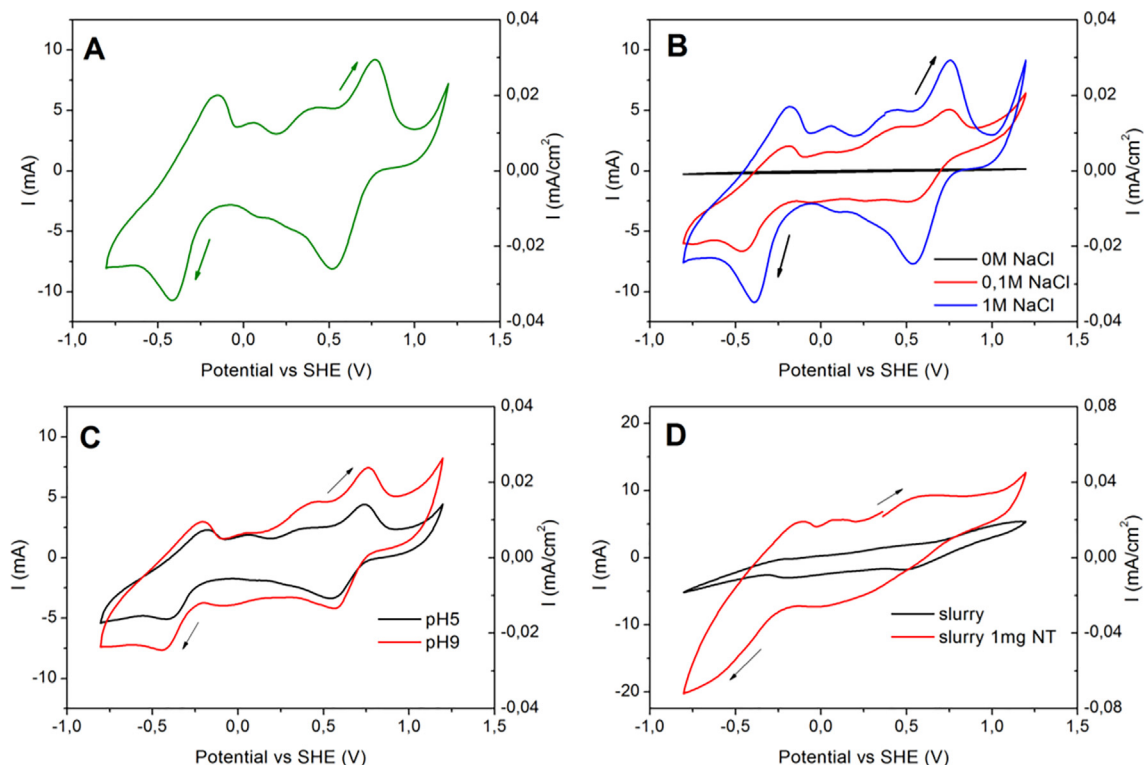
dissolved in 1 mL of water and deposited onto each porous carbon electrode in each side of the symmetric cell. After the carbon felt absorbed the CP, a 10 mL of an aqueous solution of 0.5 M NaCl was added into each electrolyte chamber.

#### 4. Results and discussion

**Fig. 2** shows the powder X-ray diffraction patterns corresponding to the CPs {[Fe(CA)(H<sub>2</sub>O)<sub>2</sub>]H<sub>2</sub>O}<sub>n</sub> and {[Mn(CA)(H<sub>2</sub>O)<sub>2</sub>]H<sub>2</sub>O}<sub>n</sub> synthesized in water and methanol. As it can be seen in **Fig. 1A** and **1B** the crystalline structure was kept in both systems, exhibiting both isostructural features after being synthesized in methanol media in comparison with the polymers prepared in water. The XRD patterns matched with the bibliographical data published enclosed at the Cambridge Structural Database (CSD) by Kawata et al. [10].

The chemical functionalities of the CPs was studied by FTIR as it is shown in **Fig. S1**. A wide vibration band corresponding to the stretching of OH group of the water molecules is observed at 3400 cm<sup>-1</sup>. Also, a band at 1500 cm<sup>-1</sup> attributed to the C=O vibration is observed in the spectra. The band appeared shifted with respect to the pristine vibration band centred at 1600 cm<sup>-1</sup> corresponding to the carbonyl group in the chloranilic acid due to the coordination of the ligand with the metal [15].

**Fig. 3** shows the SEM images of the CPs studied herein. The {[Mn(CA)(H<sub>2</sub>O)<sub>2</sub>]H<sub>2</sub>O}<sub>n</sub> (**Fig. 3A**) and {[Fe(CA)(H<sub>2</sub>O)<sub>2</sub>]H<sub>2</sub>O}<sub>n</sub> (**Fig. 3C**) hybrid materials synthesized in aqueous media exhibited a particle size of approximately 10–30 μm length, sharing also the same lamellar-like particle morphology. Interestingly, using methanol as a solvent in the preparative procedure resulted in a one order of magnitude decrease in particles size for both coordination polymers leading to



**Fig. 5.** Cyclic voltammetry measurements of the aqueous suspensions of the {[Fe(CA)(H<sub>2</sub>O)<sub>2</sub>]H<sub>2</sub>O}<sub>n</sub> polymer. (A) Cyclic voltammetry at a scan rate of 20 mV/s for the CP {[Fe(CA)(H<sub>2</sub>O)<sub>2</sub>]H<sub>2</sub>O}<sub>n</sub> with a concentration of 1 g/L in an aqueous suspension containing 0.5 M NaCl as supporting electrolyte at pH value of 7. (B) Influence of the concentration of the supporting salt on the redox processes appearing during the cyclic voltammetry analysis. (C) Influence of the pH value on the redox processes. (D) Cyclic voltammetry of a slurry containing 100 g/L of the CP {[Fe(CA)(H<sub>2</sub>O)<sub>2</sub>]H<sub>2</sub>O}<sub>n</sub> in a 2 M NaCl aqueous solution with no conductive additives (black line) and with 1 mg of carbon nanotubes (red line) at a scan rate of 5 mV/s.

2–3  $\mu\text{m}$  length particles (Fig. 3B and 3D). Light scattering diffraction (LSD) experiments carried out for an aqueous suspension (10 mg/L) showed a particle size around 200–600 nm for the iron based particle synthesized in methanol (Fig. S2).

Fig. 4 shows the results of the stability studies for the aqueous suspensions containing the coordination polymers synthesized either in water or methanol. The suspensions of the CPs synthesized in methanol media had longer-term stability, 72 h, than those synthesized in aqueous media, 8 h. This result is in agreement with the reduced sizes observed in the SEM images and also with previously published works based on the stability studies of particulate suspensions in aqueous media [16].

The electrochemical properties in aqueous media of the coordination polymers synthesized in methanol were studied by cyclic voltammetry. The concentration of the suspension containing the CPs was 1 g/L. The presence of NaCl at different concentrations as supporting electrolyte did not modify the stability of the CPs suspensions.  $\{[\text{Mn}(\text{CA})(\text{H}_2\text{O})_2]_n\text{H}_2\text{O}\}_n$  presented two well-defined redox processes at 0.9 V and  $-0.5$  V vs. SHE at neutral pH shown in Fig. S3. The reduction wave at  $-0.5$  V corresponded to the metal plating process [17] and it was not observed when shorting the potential window up to  $-0.8$  V (Fig. S3A).

Fig. 5 shows the cyclic voltammograms recorded for  $\{[\text{Fe}(\text{CA})(\text{H}_2\text{O})_2]_n\text{H}_2\text{O}\}_n$  in different conditions. The Fe-CP presented also two processes, one at  $-0.3$  V and another at 0.7 V vs SHE at a pH value of 7, but unlike the manganese polymer, no metal plating was observed near the lower potential peak as is evidenced in Fig. 5A. The plating process, along with the loss of the redox activity was observed only when the potential window was opened up to  $-1.3$  V vs. SHE (Fig. S3B). The influence of the supporting salt concentration on the electrochemical properties were also studied for both CPs  $\{[\text{Fe}(\text{CA})(\text{H}_2\text{O})_2]_n\text{H}_2\text{O}\}_n$  (Fig. 5B) and  $\{[\text{Mn}(\text{CA})(\text{H}_2\text{O})_2]_n\text{H}_2\text{O}\}_n$  (Fig. S4). In general, the addition of sodium chloride as a supporting salt to the dispersion of the coordination polymers, improved the efficiency of the redox processes, achieving a higher chemical reversibility. When the concentration of NaCl was higher than 0.5 M, a clear improvement in chemical reversibility of the redox processes was observed.

The influence of pH on the electrochemistry of the aqueous suspension containing the CP  $\{[\text{Fe}(\text{CA})(\text{H}_2\text{O})_2]_n\text{H}_2\text{O}\}_n$  was also studied (Fig. 5C). At pH = 5, the redox process at 0.7 V evidenced a low chemical reversibility, while at pH = 9 the process at  $-0.3$  V showed lower chemical reversibility. Because  $\{[\text{Fe}(\text{CA})(\text{H}_2\text{O})_2]_n\text{H}_2\text{O}\}_n$  showed the highest efficiency regarding chemical reversibility of the two processes, it was chosen as the most suitable candidate. Therefore, in order to assess the potential of this hybrid redox active material as a single electrolyte component in flow batteries, a further electrochemical characterization of  $\{[\text{Fe}(\text{CA})(\text{H}_2\text{O})_2]_n\text{H}_2\text{O}\}_n$  was done. Firstly, to maximize the amount of the CP exhibiting three-redox stages to boost the energy storage of the particulate slurry system, a suspension of the CP containing 100 g/L was prepared. The particulate slurry was characterized by three-electrode voltammetry. The redox peak processes evidenced low intensity, hence the concentration of NaCl was increased up to 2 M and carbon nanotubes at 1:100 (CNT/CP) ratio were added in order to enhance the electrical conductivity (Fig. 5D).

The assessment of using dialysis membranes as low-cost separators was checked by a permeability test carried out using an H-shaped cell. In one branch, an aqueous solution with a concentration value up to 1 g/L  $\{[\text{Fe}(\text{CA})(\text{H}_2\text{O})_2]_n\text{H}_2\text{O}\}_n$  was introduced and in the other side only deionized water was located. Two types of dialysis membranes with different pore sizes, 1 kDa (0.88 nm) and 8 kDa (1.75 nm), were tested. After 20 days, the deionized water solution was tested by UV–vis to study if there were some crossover of the  $\{[\text{Fe}(\text{CA})(\text{H}_2\text{O})_2]_n\text{H}_2\text{O}\}_n$  polymer particles (Figs. S6–S8). The test with the 8 kDa membrane obtained a concentration value up to 83 mg/L for the CP in water, while with the 1 kDa membrane no  $\{[\text{Fe}(\text{CA})(\text{H}_2\text{O})_2]_n\text{H}_2\text{O}\}_n$

was detected indicating such membrane as the most suitable one for the proposed application.

The use of single component analyte offers not only cost advantages but also eliminates the problems with membrane leakage. Our findings imply that the same electroactive material,  $\{[\text{Fe}(\text{CA})(\text{H}_2\text{O})_2]_n\text{H}_2\text{O}\}_n$ , could be used as catholyte and anolyte in a 1 V symmetrical cell at neutral or close to neutral pH. The use of aqueous electrolyte has additional advantages (cost, toxicity) and the possibility of working at neutral or close pH largely decreases corrosion issues related to other cell components. Therefore, the galvanostatic charge–discharge of the symmetrical cell using the Fe-CP as a single electrolyte for slurry based RFBs component and a porous cellulose membrane as a separator was studied. The cell was cycled for 50 cycles achieving a capacity of approximately 45 mAh/g, experiencing an irreversible capacity loss in the first cycle (Fig. 6A). The capacity loss in the first cycle can be caused by some degradation on the surface of the particles at the beginning cycling [18]. After 50 cycles (~12 days), the capacity was maintained, suggesting that the cell might be stable during more

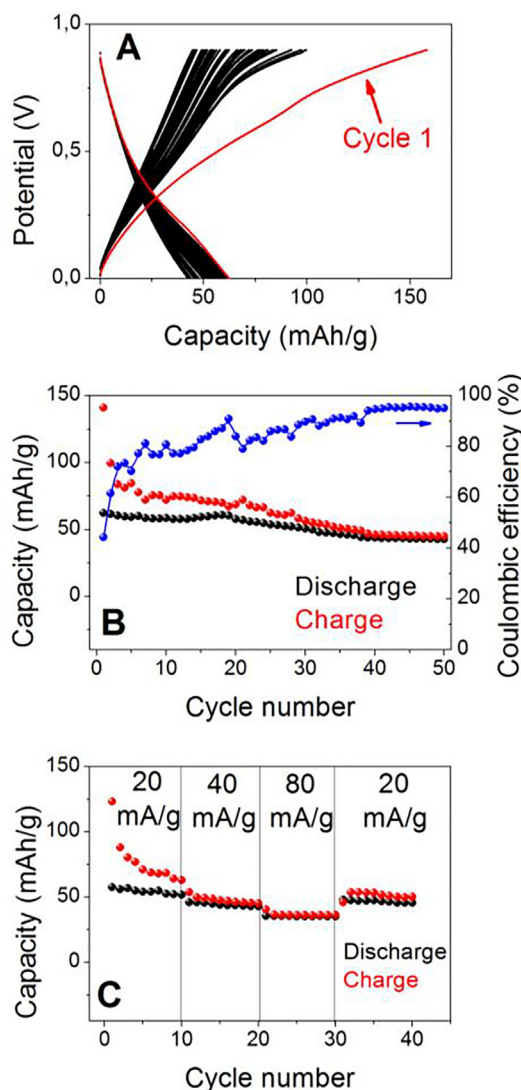


Fig. 6. (A) Galvanostatic charge–discharge profiles of the symmetrical cell cycled between 0 and 0.9 V and a current density of 20 mA/g. (B) Cycling performance and coulombic efficiency at a current density of 20 mA/g. (C) Rate capability test of the cell cycled during 10 cycles at different currents densities: 20 mA/g, 40 mA/g, 80 mA/g and again 20 mA/g.

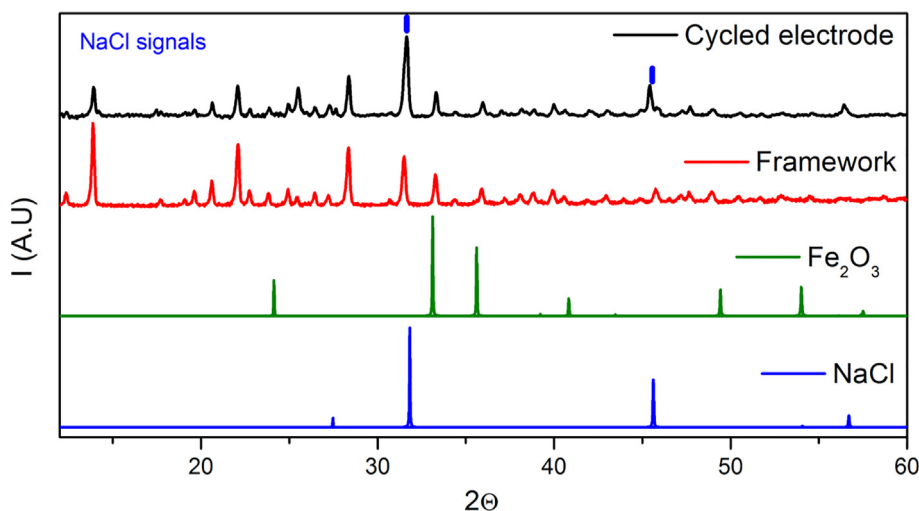


Fig. 7. XRD patterns of the electrode after cycling, the original material, NaCl and iron oxide.

extended tests, achieving a coulombic efficiency value above 90% (Fig. 6B). A rate capability analysis to test the stability of the cell at different currents was also carried out. The cell was cycled during 10 cycles at 4 different current densities, 20 mA/g, 40 mA/g, 80 mA/g and again 20 mA/g. As it can be seen in Fig. 6C, after returning to the initial current density values of 20 mA/g, the capacity was maintained, proving the stability of the cell.

In order to prove the structural stability of the material after cycling, the cell was dismantled and the electrode was studied by X-ray diffraction. The pattern showed signals of the  $\{[\text{Fe}(\text{CA})(\text{H}_2\text{O})_2]\text{H}_2\text{O}\}_n$  framework together with those due to NaCl contained in the electrolyte in combination with a broad signal at 25  $2\theta$  corresponding to the carbon felt (Fig. 7). No other signal corresponding due to a possible degradation from the framework was observed. The overall results highlight the suitability of these new frameworks to act as active materials in the development of novel redox electrolytes to overcome their current drawbacks.

Finally, Table S1 shows a comparison of the results here obtained with other reported semi-solid systems where the safety of the neutral aqueous pH of the system based on  $\{[\text{Fe}(\text{CA})(\text{H}_2\text{O})_2]\text{H}_2\text{O}\}_n$  is one of the main differences and advantages compared to other systems.

## 5. Conclusions

Water-based particulate slurries of the coordination polymers  $\{[\text{Fe}(\text{CA})(\text{H}_2\text{O})_2]\text{H}_2\text{O}\}_n$  and  $\{[\text{Mn}(\text{CA})(\text{H}_2\text{O})_2]\text{H}_2\text{O}\}_n$  were studied as potential electrolyte materials for slurry-based batteries. The synthesis of the CPs in methanol media results in small crystal size which enabled the creation of stable suspensions in water. The effect of the supporting salt, concentration, and pH of the particulate slurries on the electrochemical properties were assessed.

The most promising electrochemical activity for the CP slurries was observed for those containing NaCl as supporting electrolyte at a concentration value of 0.5 M and at pH of 7. In addition,  $\{[\text{Fe}(\text{CA})(\text{H}_2\text{O})_2]\text{H}_2\text{O}\}_n$  was the most promising CP because it did not experienced a metal plating process in the potential window selected, contrary to the metal plating phenomena observed for the  $\{[\text{Mn}(\text{CA})(\text{H}_2\text{O})_2]\text{H}_2\text{O}\}_n$  polymer.

The electrochemical study of the iron-CP framework in a symmetrical cell showed an optimum cycling stability and rate capability. From these results, we propose a proof-of concept where the new hybrid crystalline framework containing Fe might be use as potential single bifunctional analyte material in an aqueous, neutral pH, using a size-exclusion membrane as separator, for application in low-cost

batteries and other energy storage related systems. This study opens the path to future testing of coordination polymers in aqueous batteries.

## 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.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jelechem.2021.115442>.

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