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J.-M. Fontmorin, Solène Guiheneuf, P. Bassil, Florence Geneste, D. Floner. Addition of weak acids in electrolytes to prevent osmosis in aqueous organic redox flow batteries. *Electrochemistry Communications*, 2021, 132, pp.107148. <10.1016/j.elecom.2021.107148>. <hal-03420572>

**HAL Id: hal-03420572**

**<https://hal.science/hal-03420572v1>**

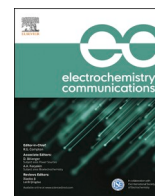
Submitted on 2 Jun 2022

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# Addition of weak acids in electrolytes to prevent osmosis in aqueous organic redox flow batteries

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## ARTICLE INFO

### Keywords:

Aqueous organic redox flow battery  
Anthraquinone-2,7-disulfonic acid disodium salt  
Ferrocyanide  
Water transfer

## ABSTRACT

Water transfer issues related to unbalanced ionic strengths in aqueous organic redox flow batteries (AORFBs) are often overlooked. In this work, a simple strategy based on the addition of a weak acid in the negolyte was studied to prevent osmosis in AORFBs. Ferrocyanide  $[\text{Fe}(\text{CN})_6]^{4-}$  and anthraquinone-2,7-disulfonic acid disodium salt (AQDS) were used as positive and negative active materials, respectively, and aspartic acid was chosen as a weak acid. The addition of acid aspartic as well as strong bases such as KOH, NaOH or LiOH to reach the complete deprotonation of the acid and the desired pH contributes to balancing the cations total concentration of both compartments. Battery cycling experiments were carried out with 0.2 – 0.3 M AQDS and 0.4 – 0.6 M  $[\text{Fe}(\text{CN})_6]^{4-}$ . When no weak acid was used, osmosis quickly leading to a shortage of negative electrolyte was observed, while in presence of aspartic acid both electrolyte volumes remained unchanged during the time of experiment.

## 1. Introduction

Ferrocyanide  $[\text{Fe}(\text{CN})_6]^{4-}$  is widely used as a positive active material in neutral and alkaline Aqueous Organic Redox Flow Batteries (AORFBs) [1–3]. In addition to being a food additive that has low toxicity for human body, it offers excellent redox reactivity and fast electron transfer kinetics [4]. However the use of  $[\text{Fe}(\text{CN})_6]^{4-}$  in AORFB electrolytes inevitably implies the addition of four molar equivalents of a counter-ion, usually  $\text{K}^+$  or  $\text{Na}^+$  (i.e.  $\text{K}_4[\text{Fe}(\text{CN})_6]$  or  $\text{Na}_4[\text{Fe}(\text{CN})_6]$ ). In addition,  $[\text{Fe}(\text{CN})_6]^{4-}$  is involved in a one-electron process while the redox reaction involving most negative active materials such as anthraquinones implies two electrons, thus requiring two equivalents of  $[\text{Fe}(\text{CN})_6]^{4-}$  in a battery. Therefore, the corresponding posolyte usually results in a much higher ionic strength compared to that of the negolyte, thermodynamically leading to severe water transfers between both tanks. Water transfer issues have already been studied in vanadium redox flow batteries (VRFBs) [5–10], but to our knowledge very little has been done for AORFBs. Although the utilisation of positive and negative electrolytes with dissymmetric volumes and concentrations can limit osmosis, this bottleneck specifically associated with the utilisation of  $[\text{Fe}(\text{CN})_6]^{4-}$  remains overlooked. In addition, the utilisation of dissymmetric tanks remains a major limitation for industrial applications (decrease of the energy density, bigger footprint, pumping requirements and energy consumption, etc). In this work, we propose a

simple strategy based on the addition of weak acids such as aspartic acid in the negolyte to prevent osmosis in AORFBs. The addition of aspartic acid as well as strong bases such as KOH, NaOH or LiOH to reach the complete deprotonation of the acid and the desired pH contributes to balancing the cations total concentration of both compartments. Battery cycling experiments were carried out with negolyte and posolyte composed of 0.2 – 0.3 M anthraquinone-2,7-disulfonic acid disodium salt (AQDS) and 0.4 – 0.6 M  $[\text{Fe}(\text{CN})_6]^{4-}$  as active materials, respectively. Cations concentrations in both compartments were followed during cycling, as well as electrolyte tank volumes to monitor the impact on water transfer.

## 2. Materials and methods

### 2.1. Chemicals and analysis

All reagents were used without further purification.  $\text{Fe}(\text{CN})_6 \cdot \text{Li}_4$  synthesis was based on [11]. Cations concentrations were measured with an Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) device (iCAP 7000Series, Thermo Scientific) under argon flux. 100  $\mu\text{L}$  samples were diluted by 10 000 in  $\text{HNO}_3$  5% prior analysis.

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<https://doi.org/10.1016/j.elecom.2021.107148>

Received 14 September 2021; Received in revised form 15 October 2021; Accepted 21 October 2021

Available online 22 October 2021

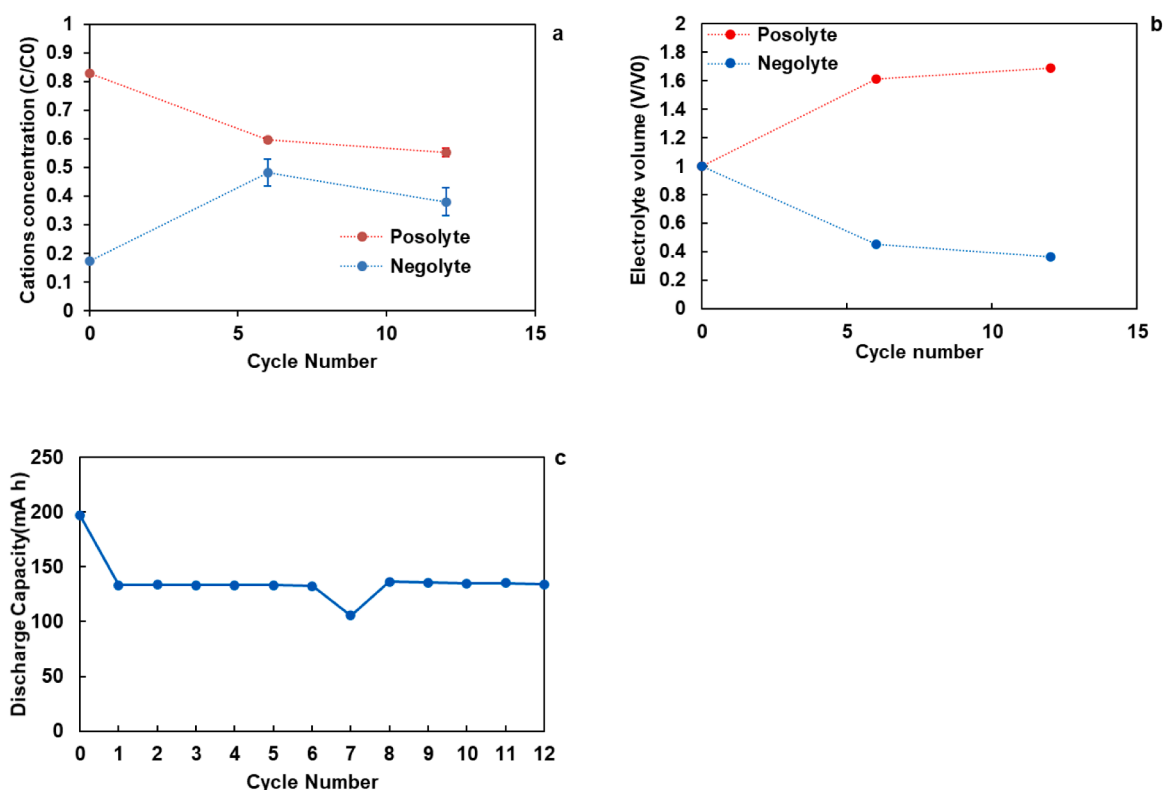
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**Table 1**  
Negolytes and posolytes formulations for experiments 1–3 and cations concentration balance (in bold) (concentrations in M).

	Experiment 1 <i>Negolyte 1</i>	<i>Posolyte 1</i>	Experiment 2 <i>Negolyte 2</i>	<i>Posolyte 2</i>	Experiment 3 <i>Negolyte 3</i>	<i>Posolyte 3</i>
AQDS disodium salt	0.2	/	0.2	/	0.3	/
Asp. Acid	/	/	0.6	/	0.9	/
Fe(CN) <sub>6</sub> ,K <sub>4</sub>	/	0.2	/	/	/	/
Fe(CN) <sub>6</sub> ,Na <sub>4</sub>	/	/	/	0.2	/	0.3
Fe(CN) <sub>6</sub> ,Li <sub>4</sub>	/	0.2	/	0.2	/	0.3
KOH	/	0.1	/	0.1	/	0.1
LiOH	0.1	/	1.3	/	1.9	/
Na <sup>+</sup>	<b>0.4</b>	/	<b>0.4</b>	<b>0.8</b>	<b>0.6</b>	<b>1.2</b>
K <sup>+</sup>	/	<b>0.9</b>	/	<b>0.1</b>	/	<b>0.1</b>
Li <sup>+</sup>	<b>0.1</b>	<b>0.8</b>	<b>1.3</b>	<b>0.8</b>	<b>1.9</b>	<b>1.2</b>
<b>Cations</b>	<b>0.5</b>	<b>1.7</b>	<b>1.7</b>	<b>1.7</b>	<b>2.5</b>	<b>2.5</b>



**Fig. 1.** Evolution of the cations concentration ratios in the negolyte and posolyte (with  $C_0$  the initial total cations concentration in the posolyte and in the negolyte) during cycling (a), evolution of the electrolytes volume ratios during cycling (with  $V_0$  the initial volume of each electrolyte) (b), discharge capacity profile during cycling (c). Formulation Experiment 1: 0.2 M AQDS (-), 0.4 M  $[\text{Fe}(\text{CN})_6]^{4-}$  (+) (details provided in Table 1).

## 2.2. Electrochemical experiments

Cyclic voltammetry analysis was performed with a Biologic SP50 potentiostat/galvanostat with a gold electrode (diameter 2 mm), a platinum wire auxiliary electrode, and a Ag/AgCl reference electrode with a salt-bridge junction in a standard three-electrode configuration. RFB experiments were carried out in a home-made cell with graphite felt electrodes (SGL carbon SE; square cuboid  $50 \times 50 \times 4.6$  mm with a geometrical surface area of  $25 \text{ cm}^2$ ; 35% compression of the thickness leading to 95.5% porosity), composite graphite current collectors and a  $50 \mu\text{m}$  cationic Nafion ion-exchange membrane. The 25 mL positive and negative electrolytes were pumped at a flow rate of  $200 \text{ mL min}^{-1}$  through KNF Pump (Liquiport® 1.100version KT). Both electrolyte tanks were graduated for the electrolyte volume to be monitored during cycling. The battery was operated through a BT-Lab V1-57 software controlling a BioLogic Science Instruments BCS 815. The cycling current density was set at  $40 \text{ mA cm}^{-2}$  both in charge and discharge and charge

and discharge voltage cut-offs were set at 1.1 and 0.6 V, respectively.

## 3. Results and discussion

Experiment 1 was carried out in absence of aspartic acid and with formulations described in Table 1.

It is known that AQDS solubility is very much impacted by its counter-ion as well as ionic environment [12]. Preliminary experiments also showed that the solubility of the negolyte in presence of aspartic acid was also impacted by the nature and concentrations of the cations. Therefore, based on literature and preliminary results on AQDS solubility in presence and absence of aspartic acid,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Li}^+$  were used as cations in various proportions in both the negolyte and the posolyte (Table 1). As can be seen, the formulation in absence of aspartic acid implies very unbalanced total concentrations of cations in the negolyte and in the posolyte (0.5 M vs. 1.7 M respectively, 2.2 M total). The results of the corresponding battery cycling are presented in Fig. 1.

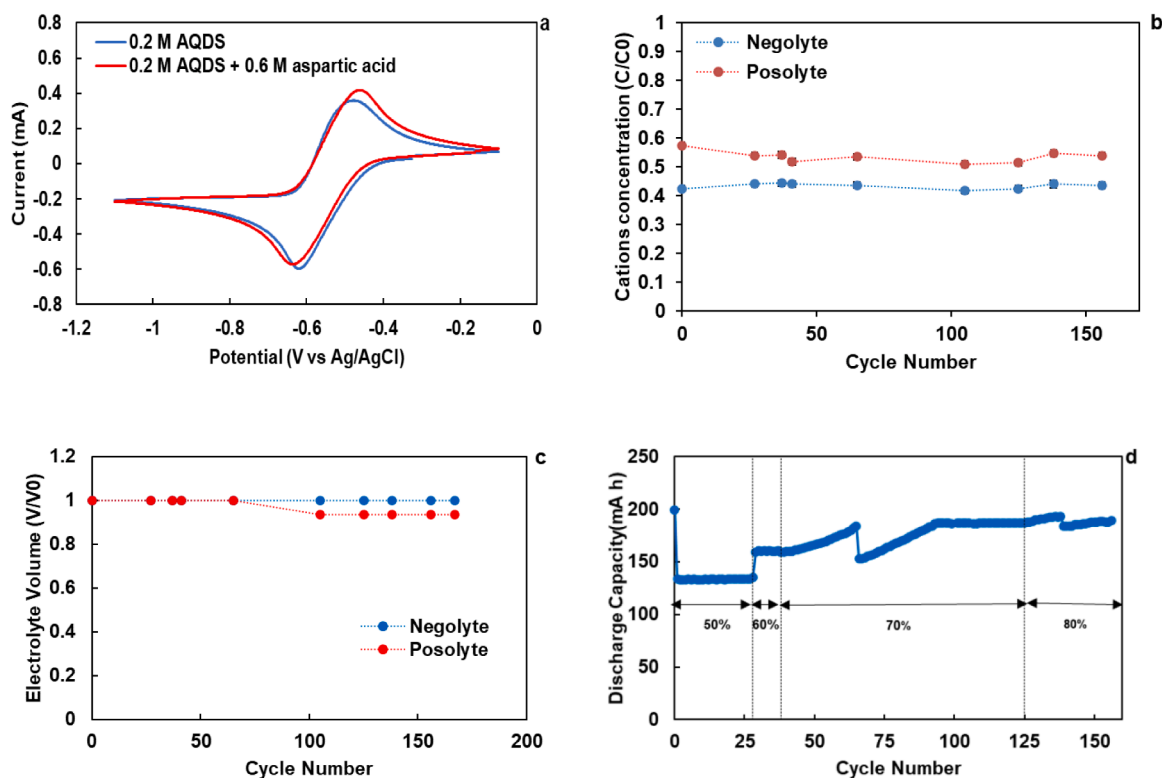
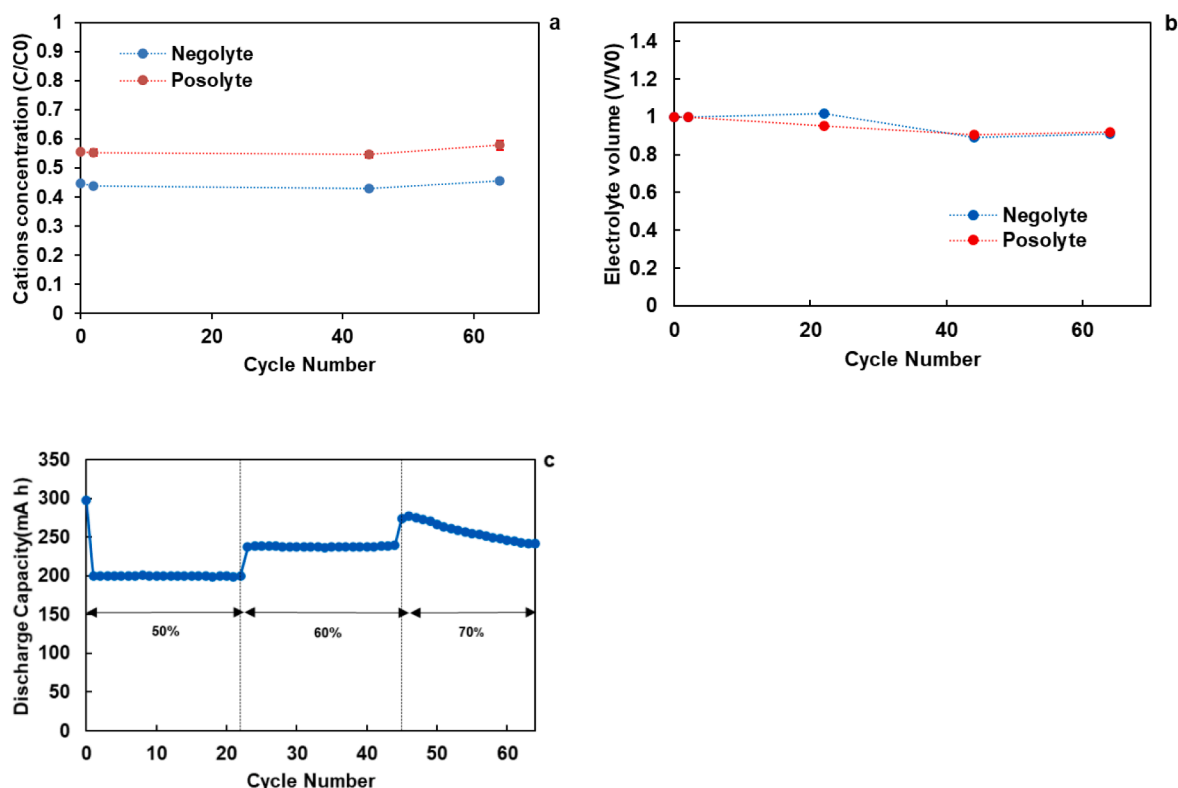


Fig. 2. 0.2 M AQDS cyclic voltammograms in absence and presence of 0.6 M aspartic acid (a). CVs recorded in 0.1 M and 1.3 M LiOH, respectively. Scan rate  $20 \text{ mV s}^{-1}$ . Evolution of the cations concentration ratios in the negolyte and posolyte (with  $C_0$  the initial total cations concentration in the posolyte and in the negolyte) during cycling (b), evolution of the electrolytes volume ratios during cycling (with  $V_0$  the initial volume of each electrolyte) (c), discharge capacity profile during cycling, with capacity cut-offs (in % vs. theoretical capacity) (d). Formulation Experiment 2: 0.2 M AQDS + 0.6 M aspartic acid (-), 0.4 M  $[\text{Fe}(\text{CN})_6]^{4-}$  (+) (details provided in Table 1).

Fig. 1.a shows the evolution of total cations concentration ratio in the posolyte and in the negolyte during cycling calculated from ICP-OES measurements (with  $C_0$  the initial total cations concentration in the posolyte and in the negolyte). As shown, the concentration ratios very quickly tend to equilibrium, with the posolyte concentration decreasing and the negolyte concentration increasing. The cations concentration equilibrium observed was concomitant with a significant water transfer from the negolyte tank to the posolyte tank, as depicted in Fig. 1.b (with  $V_0$  the initial volume of the negolyte or posolyte). After 6 cycles only, about 55% of the volume of the negolyte was transferred to the posolyte, which increased to 64% after 12 cycles only. This water transfer rapidly led to a shortage of negolyte, forcing the operator to stop battery. Fig. 1.c shows the battery discharge capacity during cycling. In order to solely focus on cations and water transfers and avoid other issues such as precipitation of the reduced form of AQDS during cycling, the maximum charge capacity was set at 50% of the theoretical value (i.e. 50% of 268 mA h). The battery could run at constant discharge capacity as long as sufficient volume of electrolyte was remaining in the negolyte tank. However, Fig. 1.b clearly shows that with such electrolyte formulations and more specifically with unbalanced cations concentrations and due to severe water transfer, the battery cycling would inevitably lead to a negolyte shortage potentially damaging the pump. Significant osmosis could also lead to the precipitation of active materials, which would obviously also be detrimental to the battery performance. In order to prevent water transfer, the electrolyte formulation was adapted (Table 1, Experiment 2). In this electrolyte, 0.6 M aspartic acid was added to the negolyte along with 1.3 M LiOH, corresponding to 1.2 M LiOH for the complete deprotonation of aspartic acid (2 carboxylic acid groups) + 0.1 M LiOH to reach  $\text{pH} \approx 13.0$ . With the addition of 0.6 M aspartic acid and 1.2 M LiOH, 1.2 M cations (in this case  $\text{Li}^+$ ) was added compared to the formulation without aspartic acid (Table 1, Experiment

1). Therefore, a balanced cations concentration was reached between the negolyte and the posolyte (1.7 M each side, 3.4 M total). The results associated with the utilisation of aspartic acid in the electrolyte are presented in Fig. 2. First and foremost, the electrochemical compatibility of aspartic acid with AQDS was checked (Fig. 2.a). The cyclic voltammogram presented in Fig. 2.a suggests that the addition of 0.6 M aspartic acid has no significant impact on the electrochemical behaviour of AQDS (0.2 M in 1.7 M LiOH), with no apparition of additional electrochemical feature that could be associated with aspartic acid. Although a slight increase of  $\Delta E_p$  (peak-to-peak potential: 142 mV and 177 mV without and with aspartic acid, respectively) can be observed, this could be attributed to a slightly higher viscosity of the electrolyte in presence of aspartic acid and additional LiOH.

Fig. 2.b shows the evolution of total cations concentration ratios in the posolyte and in the negolyte during cycling. As the negolyte and posolyte were composed of similar cations concentrations (1.7 M), similar initial ratios of 0.5 were expected. The difference measured (0.43 vs. 0.57) can be attributed to ICP measurement deviations. Nevertheless, it can be seen that equilibrium seemed to be reached from the beginning of the experiment as ratios in the negolyte and in the posolyte remained fairly constant over the time of experiment (respectively 0.44 and 0.53 after cycle 65, and 0.44 vs. 0.54 after cycle 156). This equilibrium in cations concentrations translated in very negligible water transfer throughout the experiment (156 cycles, Fig. 2.c). Indeed, no change in electrolytes volume was observed until cycle 100, after what the posolyte volume ratio only decreased from 1.00 to 0.97. These results show the positive impact of the addition of aspartic acid with the required strong base (LiOH) on water transfer during cycling. In addition, it should be noted that nuclear magnetic resonance analysis carried out on the electrolytes at the end of the experiment revealed no sign of cross-over of AQDS nor aspartic acid from the negolyte to the posolyte. Fig. 2.



**Fig. 3.** Evolution of the cations concentration ratios in the negolyte and posolyte (with  $C_0$  the initial total cations concentration in the posolyte and in the negolyte) during cycling (a), evolution of the electrolytes volume ratios during cycling (with  $V_0$  the initial volume of each electrolyte) (b), discharge capacity profile during cycling with capacity cut-offs (in % vs. theoretical capacity) (c). Formulation Experiment 3: 0.3 M AQDS + 0.9 M aspartic acid (-), 0.6 M  $[\text{Fe}(\text{CN})_6]^{4-}$  (+) (details provided in Table 1).

d shows the battery discharge capacity profile during cycling. As no water transfer was observed from the beginning of the experiment, the maximum capacity cut-off was increased progressively to evaluate the impact of the state-of-charge (SOC) on water transfer. The capacity cut-off was initially set at 50% of the maximum theoretical capacity (i.e. 50% of 268 mA h). At the end of cycle 27, as stability was observed (capacity stability of + 0.01%/cycle), the cut-off was increased to 60%. Similarly, stability was quickly reached (-0.01%/cycle) and the cut-off was thus increased to 70% at cycle 38. In this case, the capacity increased slowly to 69% before dropping back to 57% at cycle 66, and slowly increasing again to reach and stabilize at 70% at cycle 94. This behaviour can be attributed to the accumulation of the reduced form of AQDS while reaching higher SOC. The reduced form of AQDS is indeed known to be less soluble than its oxidized form, hence probably leading to the accumulation of insoluble particles within the carbon felt [13]. Nevertheless, the non-limiting flow-rate used ( $200 \text{ mL min}^{-1}$ ) is probably the reason why 70% of the theoretical maximum capacity could eventually be reached and remain stable for 31 cycles (capacity stability of + 0.004%/cycle, cycle 94–125). As shown in Fig. 2.c, very little osmosis was observed even when 70% discharge capacity was reached. From cycle 126 to cycle 156, the capacity cut-off was set to 80%, which could never be reached, as shown in Fig. 2.d. Although it was not possible to reach 80% of the theoretical capacity, most likely due to partial precipitation of the reduced form of AQDS, the addition of 0.6 M aspartic acid showed that it could effectively prevent osmosis by balancing cation concentration in both tanks. In order to evaluate the feasibility of this strategy at higher concentration, AQDS concentration was increased to 0.3 M with the addition of 0.9 M aspartic acid, hence corresponding to 2.5 M cations concentrations in the posolyte and negolyte tanks (Table 1, Experiment 3). The results associated with the battery cycling are presented in Fig. 3. As observed in Experiment 2, cations concentration equilibrium was reached from the start of cycling,

resulting from the electrolytes formulation (Fig. 1.a). This equilibrium translated into negligible water transfer, as depicted in Fig. 3.b. Both tank volumes remained constant over the time of experiment (64 cycles), disregarding the capacity cut-off set. Fig. 3.c displays the battery discharge capacity profile during cycling. Similarly to Experiment 2, the capacity cut-off was increased progressively, starting from 50% of 402 mA h (cycle 1–22) and subsequently 60% (cycle 23–44). In both cases, capacity stabilities of -0.007 and + 0.015%/cycle were measured, respectively. However, when the cut-off was increased to 70%, the discharge capacity could only reach a maximum of 277.1 mA h (68.9%, cycle 46) before decreasing to 60.1% (cycle 64).

This work has shed light on the addition of aspartic acid as a simple yet effective strategy to prevent osmosis in AORFBs with AQDS as model compound. Nevertheless, several points should be looked at into more details in order to improve this strategy. First and foremost, although aspartic acid was chosen as a weak acid to indirectly balance cations concentrations, other weak acids such as succinic acid, citric acid or ethylenediaminetetraacetic acid (EDTA) could be considered. Indeed, with respectively 3 and 4 carboxylic acids groups, lower concentrations of citric acid or EDTA would thus be required compared to that of aspartic acid. Solubility tests as well as electrochemical characterizations would be required to evaluate the compatibility of such acids with the model compound chosen. With the addition of relatively high concentrations of weak acids and strong bases, a detrimental impact on the solubility of the active material is likely. Therefore, a further optimization would also be needed to better control the concentration of weak acid required. In this work, the aspartic acid concentration was adapted so that to equal cations concentration in the posolyte and in the negolyte were reached. However, perfect equilibrium may not be needed to prevent water transfer, in which case a lower concentration of weak acid could be sufficient. On the contrary, for other model compounds, a perfect equilibrium might even lead to inverting water transfer (from

posolyte to negolyte instead of negolyte to posolyte), hence also needing optimization.

#### 4. Conclusions

This work focused on a strategy to prevent water transfer from the negolyte to the posolyte in AORFBs based on the addition of a weak acid in the negolyte. Aspartic acid was chosen as the weak acid and the required amount of strong bases such as NaOH, KOH or LiOH for its complete deprotonation was used to balance cations concentrations in the posolyte and negolyte tanks. The conclusions are as follows:

- In absence of weak acid and in presence of symmetrical negolyte and posolyte tank volumes, severe water transfer is observed quickly leading to a shortage of negolyte and precipitation issues, thus critically hindering the battery performance.
- Aspartic acid is compatible in terms of solubility and electrochemical behaviour with 0.2 M and 0.3 M of the oxidized form of AQDS.
- Balancing total cations concentrations in the negolyte and in the posolyte with the addition of aspartic acid was shown to be effective to prevent osmosis during battery cycling.
- In presence of aspartic acid and in absence of water transfer, batteries using 0.2 M and 0.3 M AQDS could reach 70% and 60% of the maximum theoretical capacity, respectively.

In order to improve this strategy, further efforts would be needed to investigate on:

- The optimization of aspartic acid concentration in order to minimize its utilization while preventing osmosis and maintaining high solubilities of both oxidized and reduced forms of AQDS.
- The utilization of alternative weak acids such as citric acid or EDTA.

#### CRediT authorship contribution statement

**Jean-Marie Fontmorin:** Conceptualization, Methodology, Validation, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Solène Guihéneuf:** Conceptualization, Writing – review & editing. **Patricia Bassil:** Writing – review & editing. **Florence Geneste:** Writing – review & editing, Supervision, Funding acquisition. **Didier Floner:** Conceptualization, Investigation, Writing – review & editing, Supervision, Funding acquisition.

#### 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.

#### Acknowledgments

The authors thank Région Bretagne (NEOBAT project), BPI France (Concours Mondial de l'Innovation) and Campus France (Bourse d'excellence Eiffel) for financial support.

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