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How anthraquinones can enable aqueous organic redox flow batteries to meet the needs of industrialization

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Abstract

Owing to the importance of storage and its hybridisation with renewable energy technologies for the energy transition, a high attention has been paid towards the development of redox flow batteries. Among all different emerging technologies, aqueous organic redox flow batteries (AORFBs) are particularly attractive since the objectives in terms of sustainability, cost and safety issues can be achieved owing to the high possibilities offered by molecular engineering, organometallic and coordination chemistry. Thus, AORFBs based on anthraquinones paired with ferrocyanide in basic medium have been widely developed and are close to reach the performances required for industrial processes. This review aims to focus on the main parameters making possible the integration of anthraquinone derivatives as negolyte in AORFB with a special attention for their implementation in industrial process.

Keywords: anthraquinone, ferrocyanide, aqueous organic redox flow battery, electrolyte, electrode pre-treatment, industrial requirements, basic medium

1. Introduction

The concept of flow battery has been early proposed with notably the publication of a functional model by C. Renard and A. Krebbs [1], involving a flowing chlorochromic solution in contact with zinc electrodes. It allowed the electric alimentation of the aerostat “La France” propeller, leading to its first flight in closed circuit in 1884. Ninety years later, began the “NASA redox storage system technologies project”, which after 10 years of study led to the development of a first battery involving the two couples $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Cr}^{3+}/\text{Cr}^{2+}$, project that greatly contributed to the international emergence of redox flow batteries [2]. Among the studied couples, all vanadium redox flow battery has attracted a lot of interest and has been largely developed by M. Skyllas-Kazacos and co-workers [3], giving rise nowadays to a reference in redox flow batteries. Thus, although redox flow batteries have been studied for a long time, the interest for their development appeared more recently. In view of the challenges posed by the storage of renewable energies, many redox active species have been successfully implemented in RFB, making them more and more promising for intermittent energy storage. More specifically, aqueous organic redox flow batteries (AORFB), whose concept began in the early 2010s [4-7], have attracted a lot of attention due to the enormous possibilities afforded by molecular engineering (and also organometallic and coordination chemistry) and the possibility to reach the objectives in terms of sustainability and cost, in safety and highly conductive electrolyte media. The large number of recent reviews attests to this enthusiasm [8-12]. Among organic redox active compounds that have proven their efficiency in AORFB, anthraquinone derivatives have been widely studied due to their possibility to exchange two electrons, their limited crossover, their chemical tenability and the relatively easy synthesis of water-soluble derivatives from a low cost skeleton. Their efficiency has been largely explored in basic medium as it allows the ionization of many

solubilizing functions and a good stability of the pH (high concentration of hydroxide ions limits pH variation due to side-reactions and to the charge and discharge process).

Since recent advances have shown increasingly high performances getting closer and closer to the industrial objectives, this review focus on the key parameters making anthraquinone derivatives possible negolytes in basic medium for AORFBs. We will discuss the main variables that can be adjusted to improve the performance of AORFBs, i.e. the solubility and the stability of the electrolyte according to the cycling conditions, the components of the electrochemical cell that can be adapted such as the membrane and the electrode material and other elements to consider for an accelerated development towards industrialization.

2.1. Suitable anthraquinone-based alkaline electrolytes for AORFB application

2.1.1. Solubility improvement

One of the key factors for industrial RFB application is the solubility of redox active species, allowing high energy density to be reached. It minimizes the auxiliaries losses and increases the system efficiency, the cycling range and nominal power density, and finally reduces the battery price per kW and per kW h, i.e. the total system price (CAPEX). Industrial requirements fix a minimum value of 20 Wh L⁻¹ as total energy density limit, corresponding to those of vanadium technology [13]. This value corresponds to the total energy density taking account both posolyte and negolyte volumes but not auxiliaries consumption. Several strategies can be used to improve the solubility of anthraquinones in basic medium: the introduction of solubilizing groups, a judicious choice of the counter-cation and the addition of a solubilizing compound.

In basic medium, several solubilizing groups such as sulfonate, carboxylate, hydroxyl and phosphonate have been used to improve anthraquinones solubility. They allow a wide range of pH to be used, according to their nature. Thus, whereas hydroxyls required strong basic medium to be deprotonated, sulfonates improve the solubility of anthraquinone at relatively low pH [8, 14]. Furthermore, the solubility of substituted anthraquinones is pH-dependent, even if the pH is significantly higher than the pKa of the solubilizing groups (Figure 1). For example, it has been shown that the solubility of 4,4-((9,10-anthraquinone-2,6-diyl)dioxy) dibutyrate (2,6-DBEAQ) was very low at pH 9 (< 35 mM) and good for higher pH (0.6 M at pH 12; 1.1 M at pH 14) [15], while its analogue with phosphonate-terminated groups exhibited a solubility of 0.75 M [16] at pH 9. However, an excess of KOH can also decrease the solubility due to the high concentration of K⁺ through the common-ion effect, as it has been shown with alizarin-3-methyliminodiacetic acid (AMA) [17]. It is worth noting that polyethylene glycol (PEG) side chains improve anthraquinone solubility as demonstrated with 1,8-bis(2-(2-(2-hydroxyethoxy)-ethoxy)ethoxy)anthracene-9,10-dione (PEGAQ), which is water-miscible in a broad pH range at a concentration up to 2.2 M [18]. However, PEG side chains induced high viscosity leading to high ASR values ranging from 1.8 to 2.2 Ω cm² when 1.5M PEGAQ was cycled in neutral AORFB.

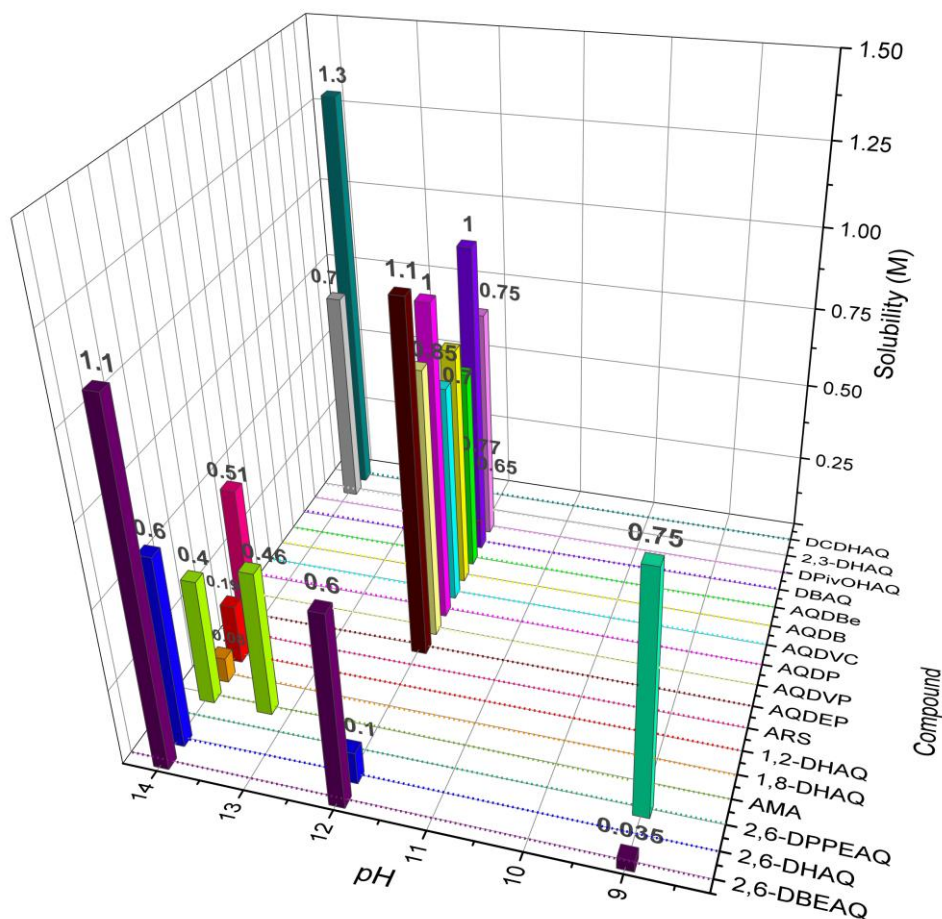


Figure 1. Solubility of 4,4-((9,10-anthraquinone-2,6-diyl)dioxy) dibutyrate (2,6-DBEAQ) [15], 2,6-dihydroxyanthraquinone [15], (((9,10-dioxo-9,10-dihydroanthracene-2,6-diyl)bis(oxy))bis(propane-3,1-diyl))bis(phosphonic acid) (2,6-DPPEAQ) [16], alizarin-3-methyliminodiacetic acid [17], 1,8-dihydroxyanthraquinone (1,8-DHAQ) [19], 1,2-dihydroxyanthraquinone (1,2-DHAQ) [19], 3,4-dihydroxy-9,10-anthraquinone-2-sulfonic acid (ARS) [13], anthraquinone-2,6-diethylphosphonic acid (AQDEP) [20], anthraquinone-2,6-divinylphosphonic acid (AQDPV) [20], anthraquinone-2,6-propanoic acid (AQDP) [20], anthraquinone-2,6-diacrylic acid (AQDVC) [20], 3,3'-(anthraquinone-2,6-diyl)dibutyric acid (AQDB) [20], anthraquinone-2,6-crotonic acid (AQDBe) [20], 4,4'-(9,10-anthraquinone-diyl)dibutanoic acid (DBAQ) [20], 3,3'-(9,10-anthraquinone-diyl)bis(3-methylbutanoic acid (DPivOHAQ) [20], 2,3-dihydroxyanthraquinone (2,3-DBAQ) [21], 1,8-dihydroxy-2,7-dicarboxymethyl-9,10-anthraquinone (DCDHAQ) [22] in KOH solution at different pH.

The position used to introduce solubilizing groups onto the anthraquinone backbone can impact the redox potential, mainly through resonance and inductive effects [14, 23]. Thus, electron donating groups such as hydroxyl directly linked to the aromatic ring of anthraquinones lead to lower potential. Electron withdrawing groups such as carboxylate, phosphonate and sulfonate should increase the potential, although it has been shown that a donor effect is obtained when sulfonate groups are in positions 1, 5 and 8 [14]. The position and number of the solubilizing groups also affects anthraquinone solubility. It has been shown that the solubility of 2,7-AQDSNa₂ is ten times higher than those of 1,5-AQDSNa₂ due to a major difference in the lattice structure and a strong Coulombic force between Na⁺ and a sulfonate group for 1,5-AQDSNa₂ [24]. The authors have also interpreted the higher solubility of 2,7-AQDS²⁻ compared with AQS⁻ (× 37) by the higher hydration energy of the divalent 2,7-AQDS²⁻. The effect of the hydroxyl position on the solubility of dihydroxyanthraquinones

in alkaline solution has been studied and it was observed that the position in 1, 4, 5 and 8 decreases the solubility, whereas β -OH groups on the anthraquinone backbone improve it [19]. The high difference of solubility would be due to the difference in pKa of α - and β -OH groups; electron-withdrawing effect of the carbonyl group induces improved proton dissociation for the β -OH groups whereas the presence of strong intramolecular hydrogen bonds between carbonyl groups and α -OH groups decreases it. Solubilizing groups were also attached on alkyl chains to enhance the solubility by frustrating crystallisation [15]. The comparison of several anthraquinone derivatives with saturated and unsaturated chains containing sulfonate, phosphonate and carboxylate ending groups has been performed [20]. The authors noticed that compounds with unsaturated chains were less soluble than those with saturated chains and explained it by the extension of the conjugation, which enhances the intermolecular π - π interactions. For anthraquinones functionalized by two carboxylate chains in position 2 and 6, they also observed a higher solubility when there are two methylene groups inside the chain instead of three and explained it by the increase of hydrophobicity. Thus, comparison of the solubility of different anthraquinones may allow some trends to be deduced, but the measurement conditions must also be comparable to draw conclusions.

The nature of the counter-cation plays also a crucial role in the solubilisation of anthraquinones containing anionic solubilizing groups. The effect of Na^+ , K^+ and Li^+ on the solubility of sulfonated anthraquinone is generally in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+$ [24, 25]. When 2,7-AQDSH₂ is neutralized with 4MgCO₃.Mg(OH)₂, its solubility was improved thanks to the high hydration energy of Mg²⁺. However, the energy lattice is also another parameter to take into account and the strong bond between Ba²⁺ and Ca²⁺ with sulfonate groups explained the low solubility observed with these cations despite their high hydration energy [24]. Phenolate and carboxylate compounds are generally more soluble in K⁺ form, as for example with 3,4-dihydroxy-9,10-anthraquinone-2-sulfonic acid (ARS), which demonstrated a solubility of 0.51 M in K⁺ against only 0.33 M in Na⁺ [13]. Ammonium salts have also proven to be efficient to solubilize anthraquinone derivatives [26-28]. Thus, whereas 9,10-anthraquinone-2-sulfonic acid sodium salt (AQSNa) and 9,10-anthraquinone-2,7-disulfonic acid disodium salt (AQDSNa₂) have lower solubility in water at pH 7 (30 mM and 0.58 M, respectively), their corresponding ammonium salts are significantly more soluble (0.5 M and 1.9 M, respectively) [28]. The authors attributed this positive effect to hydrogen bonding of NH₄⁺ with the carbonyl oxygen, enhancing the solvation of anions in water and to the hydrophilicity of ammonium cation. Interestingly, NH₄⁺ also significantly improved the solubility of ferrocyanide to 1.91 M and ferricyanide to 1.6 M, whereas 1 M was reached with a mixture of sodium and potassium salts [29]. Interestingly, the molar conductivity of NH₄⁺ is the same as K⁺, allowing its use in redox flow battery at neutral pH. Large hydrophilic cations such as tetra-hydroxyethylammonium [N(CH₂CH₂OH)₄]⁺ (TKEN) and tetra-hydroxymethylphosphonium [P(CH₂OH)₄]⁺ (TKMP) have been studied and alizarin solubility was significantly higher with TKMP (1.9 M) than with Na⁺ (0.2 M) [30]. Although, less cationic anthraquinone derivatives have been investigated, the counter-ions can also affect their solubility. Thus, in a recent study, it has been shown that 1,8-bis(3-(trimethylamino)propoxy)anthracene-9,10-dione dichloride (QAAQ) containing quaternary ammonium solubilizing groups was soluble at about 1.2 M in NaCl even in the presence of cationic (Mg²⁺ and Ca²⁺) and anionic (SO₄²⁻ and PO₄³⁻) interfering ions in neutral medium [31].

The addition of solubilizing compounds can be also a good mean to increase the solubility of redox active species in solution. Since a high number of anthraquinones are thixotropic such as 2-AQS and some AQDHs [14], it can help to prevent their precipitation into the reservoirs. Hydrotropes are known to solubilize organic compounds via molecular interactions such as π - π stacking. They allow the improvement of the solubility of anthraquinones in aqueous

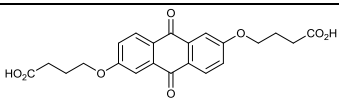
medium, also their efficiency is highly dependent on the redox active species, the pH and the electrolyte medium [32]. Thus, proline increased 2,7-AQDS solubility from 0.83 ± 0.03 M to 1.05 ± 0.23 M in acidic medium, whereas sodium xylenesulfonate (NaXS) decreased it to 0.39 ± 0.06 M. Ethylene glycol has also been used to increase the solubility of 2,7-AQDS in 1M KCl from 0.3M to 0.81M [33]. The authors explained its efficiency by the interactions between the hydrophobic backbone of ethylene glycol with the aromatic rings of 2,7-AQDS and by hydrogen bonding between its hydroxyl groups and the sulfonyl or carbonyl groups of the anthraquinone. The solubility of anthraquinone-2-sulfonic acid sodium salt has been multiplied by around 6 with urea used as hydrotrope, although the cyclability of the battery has been demonstrated with benzene-1,4-diol [34]. Our group has also shown that a small amount of ionic liquid (5-10% v/v) in aqueous medium improves the solubility of substituted anthraquinones, maintaining a good conductivity to the solution [35]. For example, alizarin (0.3M) mixed with diisopropylethylmethylammonium sulfate in 2M KOH was paired with potassium ferrocyanide (0.56 M) in AORFB, limiting the area specific resistance to $2.1 \Omega \text{ cm}^2$.

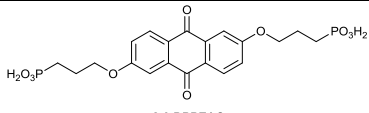
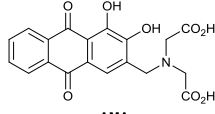
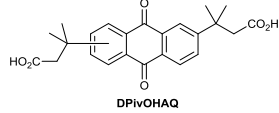
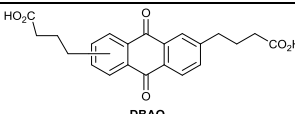
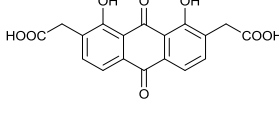
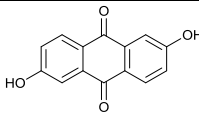
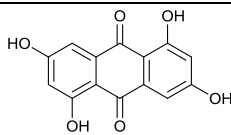
Although computational studies have predicted aqueous solubility limits of anthraquinone derivatives in the range of 2-6M [8], other constraints linked to battery operation such as ionic conductivity, viscosity and water balance limit the concentration of anthraquinones in RFB application. For this reason, demonstrated energy density in AORFB are usually lower than the theoretical ones. However, the scientific and technical barriers to be lifted are better understood and preliminary analysis can be performed to prevent battery failure. For example, the solubility of the redox active species at different states of charge can be estimated to check that it will not precipitate during cycling, since the solubilities of reduced and oxidized forms can be very different [13, 21]. The purity of commercially available compounds has also to be taken into account as it can influence their solubility [13].

2.1.2. Stability issues

A second essential requirement for industrial application is the AORFB stability. It is usually estimated through the capacity fade rate during long-cycling tests. Values $< 0.003\%$ /day for 20 years (to maintain a capacity retention higher than 80%) are expected for industrial systems to make AORFB competitive as a stationary storage system, corresponding for example to 0.003% /cycle for 1 full cycle of 10h per day [13]. High stabilities have been already reached with anthraquinone derivatives, as exemplified in Table 1. As we will discuss below, the reported values are difficult to compare due to the wide range of cycling conditions applied for each experiment. For example, the use of a glove box, high flow rates and low states of charge would favour low capacity fade rates.

Table 1. Reported performances for long cycling in AORFBs of anthraquinones derivatives with ferri/ferrocyanide as posolyte in basic medium.

Redox species	Initial pH	Concentration for long cycling (mol L ⁻¹)	Number of cycles	Fade rate (%/day) (number of days)	Degradation	Ref.
 2,6-DBEAQ	12	0.5	350	0.04 (6)	Nucleophilic substitution	[15]

 <p>2,6-DPPEAQ</p>	9-13	0.5	480	0.014 (12)	Nucleophilic substitution	[16]
 <p>AMA</p>	13.3	0.4	350	0.19 (9)	Decarboxylation	[17]
 <p>DPiVOHAQ</p>	12 14	0.5 0.5	690 690	0.014 (15.6) 0.0018 (16)	Anthrone formation	[36]
 <p>DBAQ</p>	12	0.5	650	0.0084 (15.5)	Anthrone formation	[36]
 <p>DCDHAQ</p>	14	0.2 0.75	1422 93	0.068 (23) 0.03 (9)	Anthrone formation	[22]
 <p>2,6-DHAQ</p>	14	0.2	2400	0.8 (48)	Anthrone formation	[21]
 <p>1,3,5,7-THAQ</p>	14	0.1	750	0.35 (11)	Anthrone formation	[37]

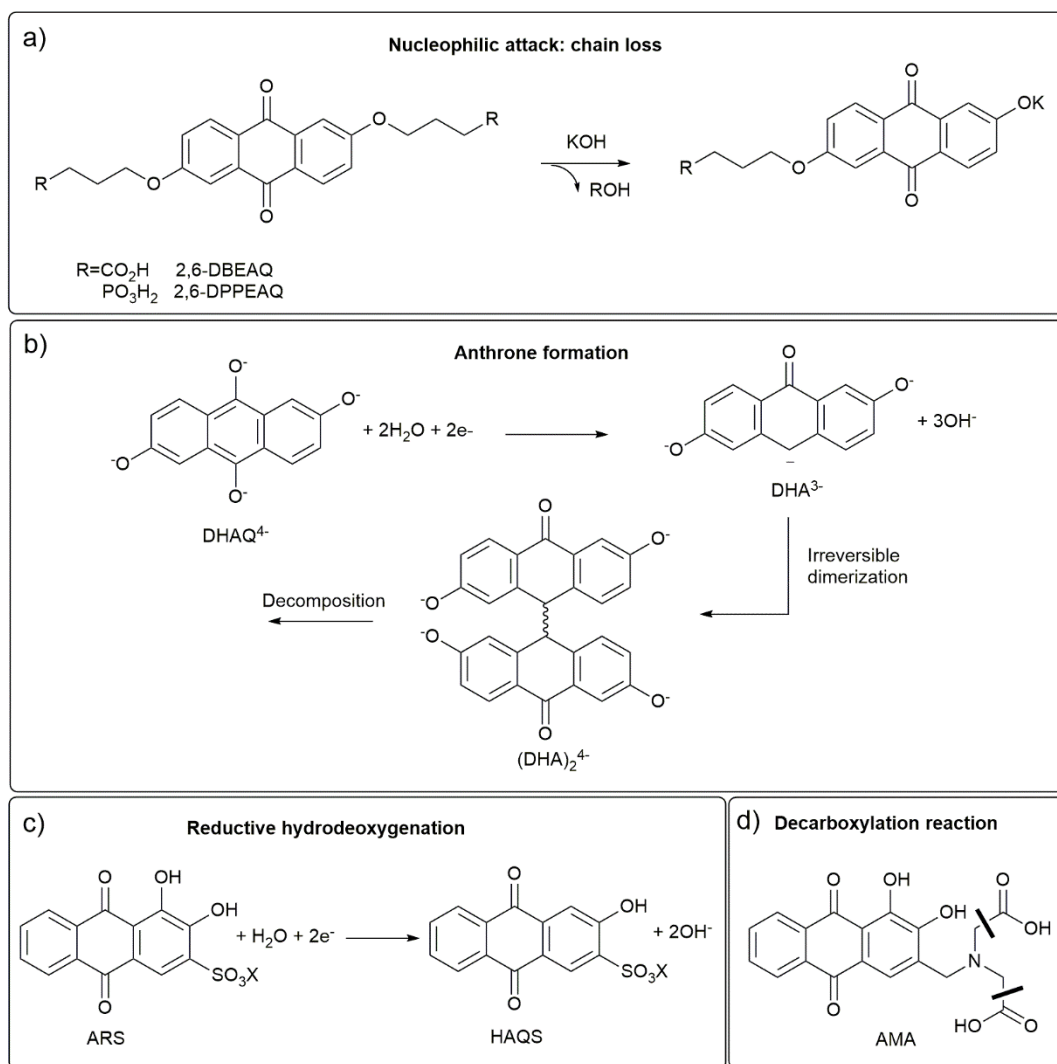
A high capacity fade rate can be attributed to exogenous and endogenous factors. Exogenous factors are sometimes not taken into account or not controlled such as the external temperature, the oxygen tightness of the process, the diffusion through the bipolar plates and sunlight exposure. Endogenous factors are inherent to the materials used *i.e.* the membrane, the active molecules and the cycling parameters. They can lead to stability issues such as the crossover of electrolyte through the membrane and the chemical decomposition of redox active species, especially the charged ones, which are generally less stable. To evaluate the AORFB stability based on this last criterium, symmetric cells have been proposed [38]. It consists in using two separate reservoirs with identical redox active species at the same concentration. With different reservoir volumes, a capacity limiting side (CLS) can be introduced, allowing a direct relationship between the fade rate and the CLS state of charge. Experiments were performed in a nitrogen-filled glovebox to prevent O₂ contamination. It has also been shown that symmetric cells combined with impedance measurement can bring important information concerning the resistance of the battery during cycling [39]. *In situ* analysis has also been developed to study the chemical stability of redox active species in RFB. Thus, on-line and operando NMR analyses have been developed to go further in the decomposition mechanism of redox active species according to the cycling conditions [40]. More data concerning the identification of unstable intermediates formed during RFB cycling have been obtained by *in situ* NMR analysis coupling with EPR analysis [41] for the detection

of radical species and with direct magnetic susceptibility measurements [42] for the determination of the state of charge.

Chemical instability of posolyte and negolyte can induce electrolyte imbalance and so capacity fading of the battery. Owing to its low cost, high stability and commercial availability, ferri/ferrocyanide is usually used as posolyte in alkaline medium, limiting the problems linked to the degradation of posolyte. However, its unstability in strong basic medium (pH 14) is still under debate [43-46]. The proposed degradation mechanism involves a CN^-/OH^- exchange reaction accelerated under ambient light exposure and a spontaneous reduction of $\text{Fe}^{\text{III}}(\text{CN})_6^{4-}$ into $\text{Fe}^{\text{II}}(\text{CN})_6^{3-}$ by free CN^- [45]. A recent study by Fell et al. suggested however that the instability of ferri-/ferrocyanide was not due to a structural decomposition but instead to the electroless reduction of ferricyanide into ferrocyanide, via electroless oxygen evolution reaction at pH above 12 [46]. The authors also proposed that this undesired reaction could be promoted by carbon surfaces, but that its prominence would decrease as the ratio of the total number of ferricyanide ions to the electrode surface area increases.

In addition to presenting instability issues at alkaline pH, the utilisation of ferrocyanide as posolyte also implies the addition of four molar equivalents of counterions, usually K^+ or Na^+ (*i.e.* $\text{K}_4[\text{Fe}(\text{CN})_6]$ or $\text{Na}_4[\text{Fe}(\text{CN})_6]$), leading to posolytes with much higher ionic strength than the negolytes counterparts. Ionic strengths imbalances thermodynamically create water transfers that can eventually lead to a shortage of negolyte. Dissymmetric tanks with higher volume of posolyte at lower concentration can limit water transfer. However, this alternative is hardly conceivable for industrial applications since dissymmetric tank volumes necessarily entail a decrease of the total energy density, a bigger footprint, higher pumping requirements and energy consumption, etc. Alternative can be considered to limit osmosis while keeping symmetric tank volumes, as adding charged additives like weak acids in the negolyte. With this simple strategy, weak acids such as aspartic acid, citric acid or EDTA can be added along with strong bases such as KOH, NaOH or LiOH to reach their complete deprotonation, maintaining the targeted pH and also contributing to balance the total cations concentrations of both compartments [47]. Using this strategy, it was shown that batteries composed of 0.2 M AQDS, 0.2 M $\text{Fe}(\text{CN})_6^{4-}$ or 0.3 M AQDS, 0.3 M $\text{Fe}(\text{CN})_6^{4-}$ with 0.6M and 0.9M aspartic acid in the respective negolytes could run with symmetric tank volumes and without water transfer. On the contrary, in absence of aspartic acid severe water transfer were observed quickly leading to a shortage of negolyte and precipitation issues, thus critically hindering the battery performance [47].

Concerning the negolyte, the degradation of anthraquinones during cycling in alkaline medium has been widely studied and reviewed (Scheme 1) [9, 11].



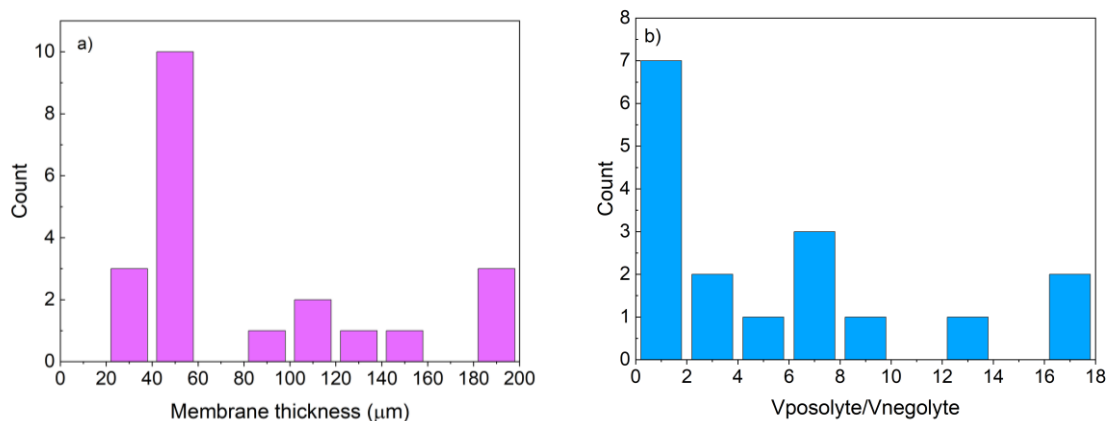
Scheme 1. Degradation mechanisms observed with anthraquinone derivatives in AORFB a) [15, 16] b) [40, 48] c) [13] d) [17]

In alkaline AORFBs, nucleophilic substitution reaction of ether chains has been observed leading to their cleavage from the aromatic ring (Scheme 1a) [15, 16]. The higher degradation at pH 14 and at elevated temperature suggested a nucleophilic attack of hydroxide ions [15]. Improved results were obtained at pH 12 leading to a capacity fade rate of 0.05%/day (0.001%/cycle) for 4,4'-((9,10-anthraquinone-2,6-diyl)dioxy)dibutyrate (2,6-DBEAQ) over a 5-day period in galvanostatic mode. It even reached 0.014%/day (0.00036%/cycle) over a period of 12 days when the carboxylate groups were replaced by phosphonate groups with (((9,10-dioxo-9,10-dihydroanthracene-2,6-diyl)bis(oxy))bis(propane-3,1-diyl))bis(phosphonic acid) (2,6-DPPEAQ), suggesting also a chemical degradation via intramolecular nucleophilic substitution by RCO₂⁻ [16]. Although carboxylate groups are efficient for solubility improvement, decarboxylation reaction can also occur as previously observed with alizarin-3-methyliminodiacetic acid (AMA) (Scheme 1d) [17]. Another important side-reaction with anthraquinone derivatives is the formation of anthrone intermediate (Scheme 1b). In a redox flow battery made by pairing 2,6-dihydroxyanthraquinone (DHAQ) with ferrocyanide, 2,6-dihydroxyanthrone (DHA) and its dimer (DHA)₂ have been identified as degradation products [48]. The authors proposed that DHA was formed by a disproportionation reaction of dihydroxyhydroanthraquinone (DHAHQ) into DHA and DHAQ. Anthrone formation has been confirmed by *in situ* NMR analysis [40]. The dependence of the decomposition on the

reduction potential suggested that the products were formed electrochemically. Similar degradation products have been identified with other anthraquinones [22, 25, 49], although strong basic medium (pH 14) [20] and low charge-limiting SOC [22, 25] seems to limit anthrone formation. Interestingly, it has been shown that anthrone can be reoxidized into anthraquinone by O₂ [48, 50] or in cycling conditions involving a low discharge potential [21, 51], allowing the possible introduction of a regeneration step during battery operation. Molecular engineering can also be a good mean to improve the stability of anthraquinone. For example, water-solubilizing groups have been introduced onto anthraquinone and anthracene as precursor, through stable carbon-carbon bonds to prevent nucleophilic substitution that occurred with heteroatom-carbon bonds. Different strategies were used such as cross-coupling reactions [20, 36] and a one-pot reaction involving the reduction by sodium dithionite of commercially available hydroxyanthraquinones and a coupling reaction with glyoxylic acid [22, 52]. No nucleophilic substitution was observed, leading to very low capacity fade rate up to 0.0084%/day at pH 12 for 4,4'-(9,10-anthraquinone-diyl)dibutanoic acid (DBAQ) [36], although the formation of anthrone always occurred. Zhu et al. synthesized an anthraquinone substituted by quaternary ammonium groups in the 1 and 8 positions [31]. Intramolecular interactions between ammonium groups and C=O/C-O⁻ induced steric hindrance and electron delocalization, preventing side reactions to occur. Thus, the reduced dihydroanthraquinone was shown to be more stable and less sensitive to dioxygen at neutral pH. The structure of anthraquinone has also an important impact on its degradation into anthrone. Thus, 1,3,5,7-tetrahydroxyanthraquinone paired with ferrocyanide did not show electrochemical dimerization during AORFB cycling in strong alkaline medium and exhibited a significantly lower capacity fade rate (0,35%/day) compared with 2,6-DHAQ (18%/day) [37]. Although most of the degradation pathways have led to non-electroactive by-products during flow battery operation, it has been shown that 3,4-dihydroxy-9,10-anthraquinone-2-sulfonic acid (ARS) was mainly transformed into 3-hydroxy-9,10-anthraquinone-2-sulfonic acid (HAQS), giving rise to a capacity fade rate of 0.29%/day (Scheme 1c) [13].

2.2. Tunable components in AORFBs

The electrode and the membrane are two tunable components that can have significant impacts on the AORFBs performance. Nevertheless, studies focusing on these components specifically for AORFBs applications are still scarce, especially compared to VRFBs. Most AORFBs studies in the literature report the utilization of commercial membranes, such as perfluorinated membranes (*e.g.* Nafion) or hydrocarbon-based polymer membranes with different thicknesses (Figure 2a).



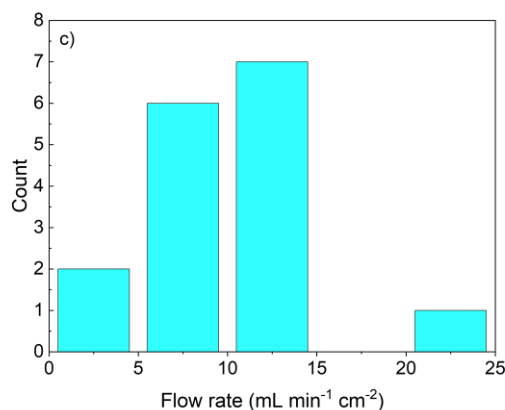


Figure 2. Distribution diagrams of membrane thickness (a), ratio of posolyte volume to negolyte volume (b) and ratio of flow rate on electrode surface (c) from recent cycling conditions [13, 15, 17, 19-22, 28, 29, 31, 33, 36, 37, 40, 41, 47-49, 53, 54] To simplify, a range of values is considered for each parameter on the x-axis.

Recently, membranes based on polymers of intrinsic microporosity (PIMs) have attracted interest for their functionalities of high permeability and molecular sieving [53]. Ye et al. developed a size selective sulfonated polymer membrane that provides improved performance in aqueous organic RFBs operated at near neutral pH conditions (pH = 9). The authors explain that the microporous structure of the membrane allows the fast and selective transport of salt ions while preventing the crossover of the negatively charged active materials, thus achieving AORFB with high efficiency and improved cycling stability [53]. Considering the very little number of studies focusing on membranes for AORFBs in basic medium and the fact that most articles involved commercially available membranes, we will not further discuss this topic in this paper. Similarly to membranes, electrode surface modification has been extensively studied for vanadium redox flow batteries (VRFBs) applications, mostly owing to the lower electrochemical reversibility of vanadium redox couples compared to that of most anthraquinones and ferrocyanide used in AORFBs. Indeed, the standard rate constant k_0 of $\text{VO}^{2+}/\text{VO}_2^+$ is about $10^{-5} \text{ cm s}^{-1}$ compared to $10^{-3} - 10^{-1}$ and $10^{-1} \text{ cm s}^{-1}$ for anthraquinone derivatives and ferrocyanide, respectively [39, 43, 55]. To date, most of the research is focusing on the development of novel and competitive electrolytes in terms of solubility and stability, but little has been done on electrode materials for AORFBs applications. However, in order to pursue the industrialization of the technology, electrode materials should not be overlooked. Despite the absence of precious metals or catalysts at the surface of their electrodes, the performance of AORFBs is not limited to the electrolytes. Electrodes impact on charge transfer, ohmics, and mass transport, but they also ensure the distribution of the liquid electrolytes and also participate to the system sealing as well as minimizing contact resistance between the cell components [56]. It was thus recently pointed out that focusing on electrode surface engineering could lead to performance and economic benefits, strongly suggesting the need to develop novel electrode materials [57]. Carbon materials are by far the most commonly used electrode materials in redox flow batteries, such as carbon papers, carbon cloths or graphitic felts. The electrode microstructure is of great importance, and Simon et al. showed that permeability, more than porosity, is a criteria of choice and indicative of performance [58]. In this context, the utilization of carbon cloth was recommended. It was also demonstrated that electrode materials with higher density of edge-like defects and oxygenated functional groups should be favored to increase the performance of AORFBs. Indeed, despite the advantageous standard rate constants of anthraquinone

derivatives for these applications, their electrochemical behaviour can be strongly affected by the carbon material structure [57]. In their study, Sedenho et al. showed for example that the electrochemical reversibility of Alizarin red S in acidic medium was highly improved using a highly-edge-density graphite electrode (HEDGE) rather than a highly ordered pyrolytic graphite (HOPG) or a glassy carbon electrode. The better performance of HEDGE was attributed to the presence of oxygenated functional groups such as C–O and C=O, and a higher density of edge-like defects. It was also suggested that the electron transfer kinetics is controlled by species adsorbed onto the electrode surface and that the adsorption is driven by the interaction between the oxygenated functions of the electrode and the functional groups of the anthraquinone derivatives [57]. Similarly to VRFBs, the performance of graphite felts for AORFBs applications can be improved *via* various pretreatments. Gao et al. showed that the electrochemical performance of commercial graphite felts could be improved *via* acid treatment, heat treatment, and combined methods [59]. The authors showed that all methods could help to improve the electrochemical performance of the graphite felt with sulfonated anthraquinone derivatives, with the air-heat treatment at 550°C for 3 hours providing the best results. In a later study, Gao et al. also investigated the response of PAN-based and Rayon-based carbon fibers, two differently manufactured carbon fibers, to chemical etching and heat pre-treatment in a DHAQ/K₄Fe(CN)₆ redox flow battery. The chemical step consisted of etching with a 0.5-1.0 M NiCl₂ before being heat-treated at 400 or 600°C for 4 to 6 hours in a muffle furnace. Both modified PAN-based and Rayon-based felts presented better electrocatalytic activity towards 1,8-DHAQ than the corresponding pristine felts, with higher current densities recorded during cyclic voltammetry. Pre-treated Rayon-based felts were the most promising materials, which was attributed to the structure of the fibers, presenting denser surface pores after etching but also more C=O functional groups than the PAN-based fibers. When implemented in a DHAQ/K₄Fe(CN)₆ redox flow battery, the pre-treated Rayon-based graphite electrodes led to a 10% increase of the coulombic efficiency compared to that of the cell equipped with pristine felts. This coulombic efficiency, however, remained relatively low (about 70%), suggesting the presence of active materials crossover or competitive reactions severely hindering the battery performance. In another study, N₂ and O₂ plasma treatment was used to improve the performance of a 2,4,5,6-tetrahydroxybenzene-1,3-disulfonic acid (TironA)/AQDS battery [60]. The electrochemical reactivity of TironA was enhanced by oxygen functional groups after O₂ plasma treatment, while it was proposed that during N₂ plasma treatment, pyrrolic and quaternary N increased the redox reactivity and electron transfer of TironA. Finally, voltage and energy efficiencies of the batteries equipped with N₂ plasma-treated and untreated graphite felts were 62% and 62%, and 58% and 57%, respectively. Surface treatment of carbon electrodes cannot only improve the electrochemical reactivity of anthraquinones derivatives, but it can also contribute to decreasing the capacity decay rate of AORFBs. It is known that anthraquinone derivatives can undergo an undesired disproportionation reaction as the battery charges to form anthrone, which is then vulnerable to dimerization [48, 54]. Interestingly, it was shown that PAN-based carbon felts oxidized thermally (600°C, 2 h) implemented in a 2,6-DHAQ/K₄Fe(CN)₆ battery could prevent the dimerization step by re-oxidizing the anthrone to the initial 2,6-DHAQ. After 200 cycles, a capacity retention of 94.42% and a capacity fade rate of 0.0287%/cycle were measured, the latter one being almost 3 times lower than that observed with untreated electrodes [54]. The thermal treatment, improving the wettability of the felt and introducing oxygen functions on its surface, thus led to higher energy efficiency and stability of the battery over time. Electrode surface treatment to improve the reactivity of K₄Fe(CN)₆ used as posolyte should not be left aside. EIS and CV analysis carried out on commercially available macro-felts and micro-fibers showed k⁰ values at least one order of magnitude higher for activated materials [61].

As described above, studies focusing on electrode surface treatment or modification for AORFBs are still scarce compared to VRFBs. It seems however possible to improve both the reactivity and the stability of the most commonly used anthraquinones derivatives as well as ferrocyanide often used as posolyte active materials. So far, thermal activation seems the most promising pre-treatment method. Methods already studied for VRFBs are yet to be explored for AORFBs, such as metals/nanoparticles deposition, graphene functionalization, electrochemical activation, etc. [62]. Nevertheless, the literature still lacks of long term cycling experiments to evaluate more in depth the stability of modified electrodes. Finally, the impact of such surface modifications on the levelized cost of storage (LCOS) should also be assessed, eventually.

2.3. How to make our research more industry-oriented?

2.3.1 Cycling parameters and reporting

Owing to the number of parameters involved in the cycling of an AORFB, it is very difficult to compare studies and performances reported in the literature, and it is even more challenging to evaluate the potential of a specific system for industrialization. In section 2.1.2, we mentioned the common utilization of excess charge/volume for the posolyte as seen in Figure 2b. Using dissymmetric tank volumes and excess charge in the posolyte can be very relevant for low technological readiness level (TRL) studies, as it allows to mainly focus on the negolyte limitations by minimizing the impact of the posolyte on the capacity decay [63]. From an industrial point of view, it is however necessarily detrimental to the overall energy density (Wh L^{-1}), which should be expressed according to the total volume of both the negolyte and the posolyte. In addition to the impact on the energy density of the system, dissymmetric tanks seem rather unrealistic for industrial applications due to the additional consequences on total footprint, pumping requirements and energy consumption. Therefore, to date, achieving high cycling stability without negatively impacting on the overall energy density remains a conundrum.

Another crucial parameter strongly impacting AORFB performance is the flow rate, and in that respect, literature is also very heterogeneous. A high number of studies report flow rates of 60 mL min^{-1} and above, which can artificially shadow some operational issues such as precipitation of active materials, mass transport limitations and underestimate the total resistance of the system. High flow-rates can also induce artificial stirring of the electrolyte in the reservoirs, hence improving mass transport, which is unlikely to happen at large-scale applications, which are on the contrary more subject to sedimentation issues. One can suggest that it would be more relevant to report flow rate per surface unit, *i.e.* in $\text{mL min}^{-1} \text{ cm}^{-2}$ so that flow rates and their impact on the performances reported would be more readily comparable (Figure 2c). The obvious limit to this is that pressure drops of the system are not taken into account. Aiming for an industrial application, a flow rate ranging from 0.6 to $1.2 \text{ mL min}^{-1} \text{ cm}^{-2}$ appears as a representative target, although these values are far from the usual conditions used at laboratory scale (Figure 2c). Therefore, although the utilization of electrodes of small surface areas can be appropriate for lower TRL studies, the flow rate should then be adjusted accordingly for a more relevant system. The type of pumps used for lab-scale experiments can also strongly impact the performance of the battery and overestimate its viability at larger scale. For example, membrane and peristaltic pumps are, to some extent, less sensitive to precipitation issues or viscosity variations than magnetic pumps used at larger scale, and they are thus able to maintain a constant flow-rate while shadowing phenomena that could potentially be critical in an industrial application. In addition, the cell inlet section to electrode

surface area ratio is often much higher at laboratory scale than it is in large scale battery stacks. Small inlet section to surface area ratios are also more prone to clogging, hence another parameter to bear in mind when evaluating electrolytes/batteries performance.

In the case where the battery cycling is not carried out in a temperature-controlled environment (which would be very energy consuming for a full-scale application anyway), monitoring the cell/electrolyte temperature brings valuable insight on the performances, especially when it comes to the area specific resistance (ASR). The accessible capacity and the energy efficiency are subject to day/night variations, which are often directly correlated to ASR variations with the temperature. With long-term cycling, performances are also subjects to seasonal variations and it is common to observe the ASR varying by tenths of $\Omega \text{ cm}^2$ as the temperature increases or drops by a few degrees. In addition, temperature impacts other important parameters such as electrolyte viscosity or active materials solubility.

Another key parameter is the limitation of the shunt current. This “current leakage” is induced by fluidic communication with a plurality of inlet and outlet distribution channels that are in fluidic communication with a bipolar plate. It causes coulombic and efficiency losses and may provoke unwanted side reactions *i.e.* redox active material degradation and water splitting during the battery operation [64]. This phenomenon is highly dependent on the stack design, the applied current, the cell potential and the number of cells. Most studies reported in literature involve vanadium-based electrolytes [65] and very scarce results are available for organic compounds.

Finally, to better assess the performance of the battery, cycling at constant power should be preferred to constant current. Indeed, the accessible capacity in particular and the overall performance of the battery in general are more representative of real-life applications when cycling is carried out at constant power. During a discharge at constant power, the current density increases as the cell voltage decreases, thus limiting the accessible capacity compared to a cycling at constant current.

Beyond the importance of cycling parameters during the experiment itself, there is a need to standardize reporting of performance metrics in the literature [63, 66, 67]. As described in the very insightful review by Li at al., important cycling parameters such as SOC, current density/voltage amplitude, cut-off voltage/current/capacity, electrolyte concentration, electrolyte volume, thickness and area of membrane and electrode, designs of flow field, testing environment in the ambient air or an inert glovebox, testing temperature and flow rate should be clearly reported [63]. Finally, several journals have established checklists to help standardize reporting for better evaluations and comparison of battery papers, with the common aim to promote transparency and reproducibility [67]. These general guidelines should, without a doubt, raise awareness of the authors and contribute to make more efficient and fruitful research for the field of AORFBS.

2.3.2. Economical aspects

A target cost of 150 \$ kWh^{-1} for 4h of storage (CAPEX) was set by the US Department of Energy [68]. This target cost comprises various parameters from engineering to raw materials costs [69]. The cost of a system is mostly driven by the electrolyte and the stack (especially the membrane, which represents ~20% of the stack cost [70]). Anthraquinone based electrolytes are usually described as low-cost materials, however, few thorough studies have been reported regarding that aspect. Dieterich et al. published the case study of the anthraquinone-2,7-disulfonic acid and compared several methods classically used to estimate the production costs depending on the state of maturation of the technology [69]. They observed that simple methods are easy to apply but lack of accuracy whereas more advanced

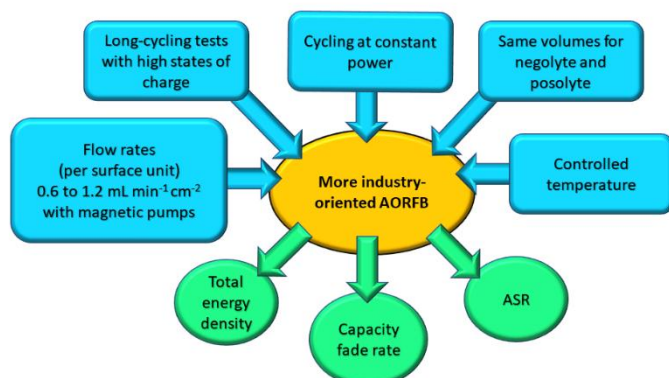
methods can lead to a better estimation but often suffer from the difficulty in accessing some information, especially for uncommercialized compounds. The authors showed that the targeted price of 5 \$ kg⁻¹ (for active species bearing a molar mass of ~150 g per mole of stored electron) can be reached in the case of AQDS but without considering the suitability of all isomers since no purification process is taken into account. Another difficulty is related to the high fluctuation of raw materials prices (precursors, solvents...) and such prediction have to be considered with great caution. Gregory et al. proposed cost and price projections of several anthraquinone derivatives (2,6-AQDS, 2,6-DHAQ, 2,6-DBEAQ and DPivOHAQ) and announced a cost close to 25 \$ kWh⁻¹ for derivatives with simple production processes (2,6-AQDS and 2,6-DHAQ) at an annual production volume of 10 GWh yr⁻¹ considering the whole system, representing 40,000 to 50,000 Million Metric Tons (MTA) for a 1.5 V average cell voltage, which is hardly achievable in an aqueous electrolyte environment without risking water splitting side-reaction [71]. Eventually it leads to a total cost of ~50 \$ kWh⁻¹ when paired with ferrocyanide based posolyte. They established that in order to reduce the global cost, redox organic molecules should match several requirements as a low equivalent weight (< 100 g per mole of stored electron, which is difficult to reach for water-soluble anthraquinones) and should allow a cell voltage as high as possible (>1V). The production of such materials should be implemented in existing production and should limit the use of organic solvents. Most of the considered synthetic routes start from anthraquinone obtained from the oxidation of anthracene (< 1 \$ kg⁻¹) [71] but the recent work of Wu et al. proposed to functionalize the anthracene scaffold before the oxidation [36]. Several strategies can be considered to level the cost by compensating the capacity fading through the replacement of active species, the separation of degradation products or the elimination of the crossover [72, 73]. In the first case, technological drawbacks would lead to an increase of the cost (recovering of the degraded products, addition of active materials...) and this additional cost should not exceed 10 \$ kWh⁻¹, but this value is submitted to the exchange rate fluctuations at the time of the additional expense. In the second case, the development of high selectivity membranes could be promoted but could likely increase the system cost as well. Promising alternatives have been reported in order to reduce the cost of the negolyte as the possibility to recover the capacity loss during operation by regenerating the electrolyte in the case of anthrone formation [21, 51]. This method could be included in the control program and would not require any external intervention, thus limiting the OPEX increase. Ultimately, one of the most efficient way to reduce the system cost is to develop highly stable molecule and to use suitable operating conditions with the possibility to regenerate or recycle the electrolytes [73]. The cost can also be reduced by the use of basic medium as it is less corrosive than acidic media therefore friendlier to the process materials in contact with the electrolytes (i.e. gaskets, pump parts, tanks...), expending their lifetime hence minimizing the OPEX (i.e. materials replacement). Furthermore, as discussed above, the stability of the electrolytes as dimerization or self-assembling behavior are lessened [74]. This higher stability of the electrolytes minimizes issues like precipitation causing flow rate fluctuation, which promotes local overpotentials therefore inducing secondary reactions (i.e. water splitting) harming electrolytes and materials [75]. Interestingly, academic developments have been performed in various pHs and recent reports tend to focus on basic media.

AORFBs have aroused a great interest and their industrialization has already begun with companies such as CMBlu (Germany), JenaBatteries (Germany), Kemiwatt (France), Lockheed Martin (USA) and Quinoenergy (USA). Several patents regarding the use of anthraquinones in aqueous alkaline media, mostly concerning their solubilization, are pending: WO2022136704 A1 (CMBlu), WO2019068920 A1 (CMBlu), WO2021193594 A1 (NIPPON KAYAKU KABUSHIKIKAISHA), WO2021123334 A1 (Kemiwatt),

WO2019157437 A1 (Harvard), WO2020072406 A2 (Harvard), WO2016144909 A9 (Harvard), US20180097249A1 (Southern California), WO2017212179 A1 (ISCR). Institutional initiatives have also been made to promote the technology maturation for implementation on the market as for example the announcement of the US Department of Energy for the creation of a national Research and Development center into long-duration energy storage at Pacific Northwest National Laboratory (PNNL), expected to be open by 2025, and a competitive award process for flow battery system research and development projects with up to US\$20 millions of funding available [76].

3. Conclusions

The growing understanding of the relationships between anthraquinone structures and their solubility allows scientists to be close to the industrial objectives in terms of energy density. However, they also have to take into account the cost of the synthetic material, which can be difficult to predict at the laboratory scale and limits the nature of reactants and the number of chemical steps. Changing the counter-cation nature and adding well-selected additives can also be a cost-effective alternative to enhance anthraquinone solubility in water. It is particularly relevant if the additives contain protonated groups that can balance the high amount of charges brought by ferrocyanide usually used as polysolite in basic medium. Concerning the stability issues, *in situ* analysis is a growing field, facilitating the elucidation of degradation mechanisms and guides molecular engineering to more stable structures. Among reported degradation processes, anthrone formation has been identified as the main degradation route of anthraquinones, although the degradation rate is highly pH and structure dependent. Interestingly, some anthrones can be reoxidized into anthraquinone starting material, constituting an easy-to-implement regeneration step. Furthermore, very promising values of capacity fade rates close to the industrial expectation have been already reported, underlining the high stability that can be achieved with anthraquinones. While experiments reported in literature are usually carried out in AORFB single cells, supplementary constraints in terms of flow rate, electrode size, shunt currents and high volumes of electrolytes exist in industrial systems. These constraints can introduce new solubility and stability issues, impacting the performance of the battery. Thus, new low cost, highly water-soluble and stable redox active electrolytes, and their implementation in a single cell taking into consideration the industrial constraints as illustrated in Figure 3 are still important research areas to be developed for AORFB application.



High topics for AORFB

- ✓ Membranes for AORFBs at different pH (low ASR, good selectivity, high stability)
- ✓ Electrode pre-treatment (kinetic, ASR)
- ✓ High solubility at different states of charge and with time
- ✓ Temperature effect (ASR, solubility)
- ✓ Studies on shunt current for AORFBs
- ✓ High cycling stability with high energy density
- ✓ Low cost synthesis and electrolyte regeneration
- ✓ New nosolvte for $7 < \text{pH} < 14$

Figure 3. Parameters for more industry-oriented AORFB tests and work perspectives

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