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Low-cost water-in-salt electrolytes for electrochemical energy storage applications: a short review

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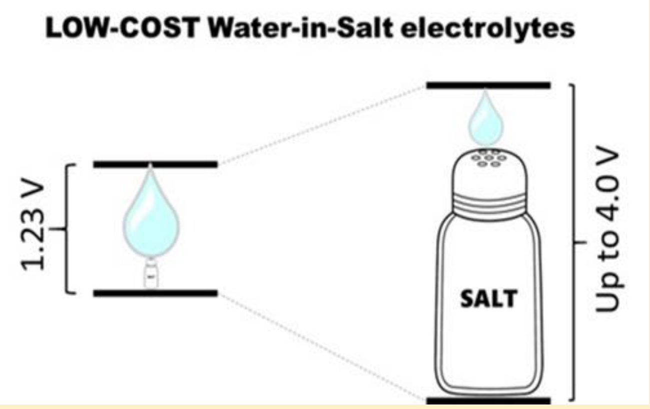

ABSTRACT: The utilization of aqueous electrolytes is an emerging field in batteries and supercapacitors to overcome the safety concerns about the flammability of the typical organic electrolytes employed in these devices. Yet, aqueous diluted electrolytes limit the electrochemical stability window (ESW) restricting the device cell voltage. Surprisingly, the use of water-in-salt electrolytes (WISEs) has demonstrated the capability of suppressing the free water content of solution leading to an ESW expansion. On the other hand, since the first report of WISEs, most of these electrolytes have employed expensive salts for their preparation, hindering the replacement of the current electrolytes, utilized in energy storage devices, by WISEs. On the other hand, in recent years, the employment of low-cost salts for WISEs has been investigated as a strategy to circumvent these economic issues revealing to be feasible for widening the cell voltage. Herein, we summarize the recent progress and developments of WISEs produced with low-cost salts providing the challenges and perspectives toward their application in electrochemical energy storage.

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1. Introduction

Since the pioneering work of Suo *et al.* (2015), water-in-salt electrolytes (WISEs) have attracted much attention in the field of electrochemical energy storage (EES) by allowing the use of aqueous electrolytes in Li-ion batteries (LIBs). However, Smith and Dunn (2015) highlighted the cost of the salt used by Suo's group to prepare their WISEs, suggesting the investigation of less expensive salts to produce such electrolytes. The insights of this work were readily accepted by the scientific community that started to explore different strategies to overcome this cost issue. WISEs are simply formed by dissolving a large amount of salts, in general, more than 5 molal (mol kg^{-1}) into water (Gambou-Bosca and Bélanger, 2016; Suo *et al.*, 2015). At these high salt concentrations, the activity of water is suppressed, and the electrochemical stability window (ESW) can be broadened up to 4.0 V, exceeding by far the thermodynamic limit of water decomposition of 1.23 V. This enhancement in ESW leads to EES devices, such as batteries and supercapacitors, with wider cell voltage, an important parameter to improve their energy density. Although the improvements in ESW by using WISEs in comparison with typical diluted solutions, the main advantage of these solvents is their non-flammable nature, which makes them promising to replace the current organic electrolyte used in Li-ion batteries and supercapacitors. Yet, to promote the large-scale application of WISEs their costs need to be competitive enough to allow their applications mentioned above. In the early developments, WISEs were mainly composed of lithium salts with fluorinated organic anions, such as lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) (Gambou-Bosca and Bélanger, 2016; Suo *et al.*, 2015; C. Yang *et al.*, 2017). The scarce content of lithium in Earth's crust and the technical issues in preparing such anions (TFSI$^-$) make this salt costly compared with the traditional organic electrolytes. In a brief search for analytical grade components of both electrolytes, 10 g of LiTFSI has an average price about 90 USD, while 100 mL of 1.0 mol L^{-1} LiPF$_6$ in propylene costs approximately 150 USD. Nevertheless, this amount of 10 g of LiTFSI only allows preparing a few milliliters of WISE. Therefore, the development of cost-effective WISEs has been a constant challenge for many scientists around the world to extend the utilization of these promising electrolytes. In this review, we discuss and explore the recent efforts on the development of low-cost WISEs for energy storage purposes and enumerate opportune strategies to circumvent their status. Specifically, the fundamental aspects of WISEs are discussed in terms of their preparation and characteristics. The concepts of water-in-single-salt-electrolyte (WISSE) and water in bi-salt electrolyte (WIBSE), as well as their state-of-the-art, are also provided. Additionally, the current trend in redox-active WISEs are reviewed. Regarding WISEs application, their utilization in EES devices is discussed besides some future directions and perspectives in order to boost their use in both academia and industry.

2. Brief fundamental aspects

The preparation of WISEs is simply done by two main components: water and salt. Yet, the salt must meet the high solubility requirement to be an eligible candidate for preparing this kind of electrolyte. Most of the highly soluble salts are composed of cations and anions with a large difference in their sizes. For instance, alkaline chlorides have the highest solubility for LiCl (~20 mol L^{-1}) which has a ratio cation/anion size of 0.53, while NaCl (~6 mol L^{-1}) and KCl (~ 4.4 mol L^{-1}) shown 0.69 and 0.91 of ratio, respectively. Additionally, RsCl and CsCl show higher solubility than that of KCl. Also, such a tendency is not observed for acetates that display the crescent solubility following the sequence KAc>NaAc>LiAc. Despite the solubility of several salts being easily found in Handbooks, the lattice and hydration energy play important roles in the future development of novel WISES since these energies are directly related to the salt solubility.

As expected, these salts need to dissociate in water forming ions that work as charge carriers in the electrolyte. Contrary to dilute solutions where those ions are surrounded by a high content of water molecules forming the solvation sheath, in WISEs the ions experience unusual ion solvation due to the low water content in the solution. Figure 1a shows a schematic of the microscopic structure of ions in dilute (salt-in-water) and high concentrated (water-in-salt) solution for LiTFSI salt (Suo *et al.*, 2015). It is seen that water molecules are arranged around the Li$^+$ in salt-in-water, while in WISE there is the formation of ions pair clusters solvated by a few water molecules. Due to the low water content in WISE, the free H_2O molecules are scarce in solution leading to a high stability potential window of the resulting electrolyte. Notwithstanding the suppression of the water-splitting reactions in WISE, the formation of the ion pair decreases the ionic conductivity of the electrolyte (Chava *et al.*, 2020; Lim *et al.*, 2018), as shown in Fig. 1b, which is a drawback to achiev high power density in energy storage devices.

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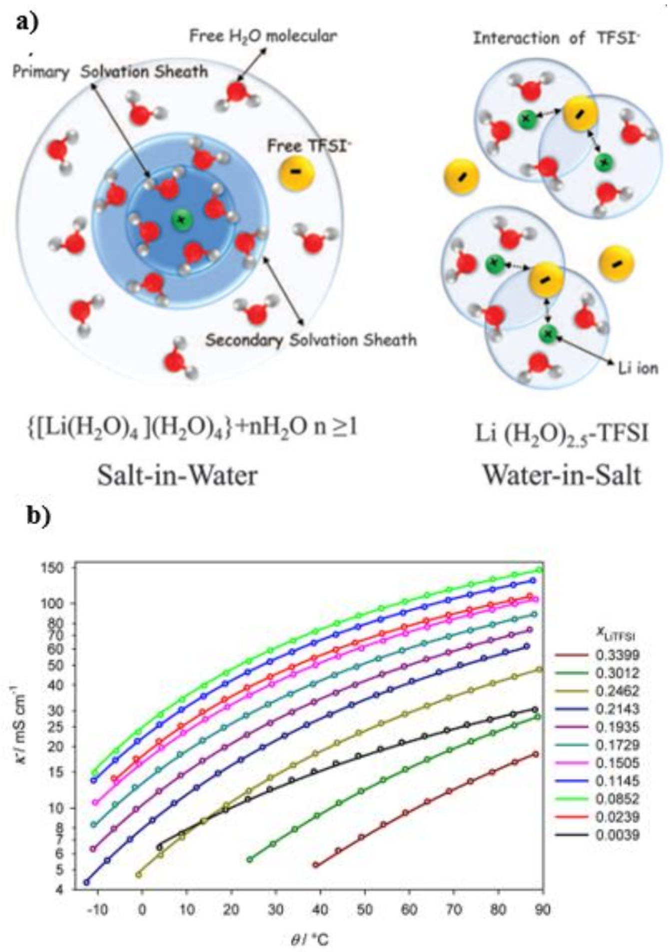

Figure 1. (a) Scheme of the Li+ first solvation sheath in salt-in-water and water-in-salt solutions (Suo *et al.*, 2015); **(b)** Ionic conductivity vs. Temperature for LiTFSI electrolytes in various mole fractions (Ding and Xu, 2018).

Source: from Suo *et al.* (2015) and Ding and Xu (2018) with permission from the American Association for the Advancement of Science and Journal of American Chemical Society, respectively.

3. Water in single salt electrolyte (WISSE)

When WISEs are prepared with only one salt dissolved in water, they have designated water-in-single-salt electrolyte (WISSE), which is the most common form observed in the current literature. WISSEs were the former concept of this class of electrolytes demonstrated by Suo *et al.* (2015), however, one year later a variant containing two salts, called water-in-bisalt electrolyte (WIBSE), was developed by the same authors (Suo *et al.*, 2016). In this section is explored the low-cost WISSEs (LC-WISSEs), displaying their drawbacks and advantages.

The same idea employed to LiTFSI was applied to different alkaline salts, e.g., acetates (Chen *et al.*, 2020a; b; J. Han *et al.*, 2018; 2020a; b; Leonard *et al.*, 2018; Lukatskaya *et al.*, 2018; Stigliano *et al.*, 2021; Thareja and Kumar, 2021), formats (T. Liu *et al.*, 2019; S. Liu *et al.*, 2022), perchlorates (Bu *et al.*, 2019a; b; Dou *et al.*, 2019; Serva *et al.*, 2021; Thareja and Kumar, 2021; Y. Zhang *et al.*, 2022), and nitrates (Adil *et al.*, 2022; Chen *et al.*, 2021; Guo *et al.*, 2019; Thareja and Kumar, 2021), and most of them also allow the extension of the potential window, but with lower costs compared to those of Li-based salts. Even though Lithium salts are the most studied due to their current application in LIBs, only its chlorides and perchlorates can be used to prepare solutions with >8 mol kg^{-1} concentrations. Yet, LiCl WISSEs have only a few studies for supercapacitor applications (Y. Zhu *et al.*, 2022). M. Lee *et al.* (2019) evaluated some typical Li and Na salts, such as sulfates, nitrates, and perchlorates for preparing WISSEs. Despite the high solubility of the nitrate, only the sodium perchlorate solutions, close to the saturation condition, displayed Raman band characteristics of water-in-salt behavior (Fig. 2a). Also, the authors performed linear sweep voltammetry in electrolytes with different contents of $NaClO_4$ to evaluate the ESW onto gold electrodes, showing that an increase of the concentration from 1 mol kg^{-1} up to 17 mol kg^{-1} of this salt permits to enlarge of the ESW in 1.0 V, reaching 2.7 V in supersaturated conditions. This value of ESW is consonant to that acquired by Bu *et al.* (2019a) which found 2.8 V (Fig. 2b) by using stainless steel electrodes in 17 mol kg^{-1} $NaClO_4$ electrolyte. Yet, in these two studies, the Raman spectra of sodium perchlorate WISSE display a broader band at 3200-3500 cm^{-1}, instead of only a sharp peak (~3550 cm^{-1}) as observed for 21 mol kg^{-1} LiTFSI electrolyte, which suggests the presence of free water molecules. Even if the molar ratio cation/water of LiTFSI and $NaClO_4$ WISSEs is similar, the presence of free water molecules in the latter is a drawback. For instance, LiTFSI WISEs were employed in LIBs with metallic lithium anode (C. Yang *et al.*, 2017) and demonstrated its low reactivity in this WISE. To the best of our knowledge, sodium perchlorate WISSEs have not been evaluated as its reactivity to alkali metals and previous reports describe the infeasibility of its direct use in conventional WISE (Im *et al.*, 2021). However, the $NaClO_4$ WISSE was applied to Na-ion batteries constructed with $NaTi_2(PO_4)_3$ anode and $Na_4Fe_3(PO_4)_2(P_2O_7)$ cathode, displaying a 2 V cell voltage with long-term stability over 200 cycles (M. Lee *et al.*, 2019). This electrolyte was also applied to carbon-based symmetric supercapacitors (Bu *et al.*, 2019a) and exhibits a working potential window of 2.3 V for the assembled device with specific capacitance

(C_{sp}) ca. 30 F g^{-1}. Moreover, Ragone plot normalized by the electrolyte prices (Fig. 2c) reveals a better cost-benefit ratio for $NaClO_4$ than that of LiTFSI WISSE, indicating that such perchlorate is a promising candidate for low-cost electrolytes.

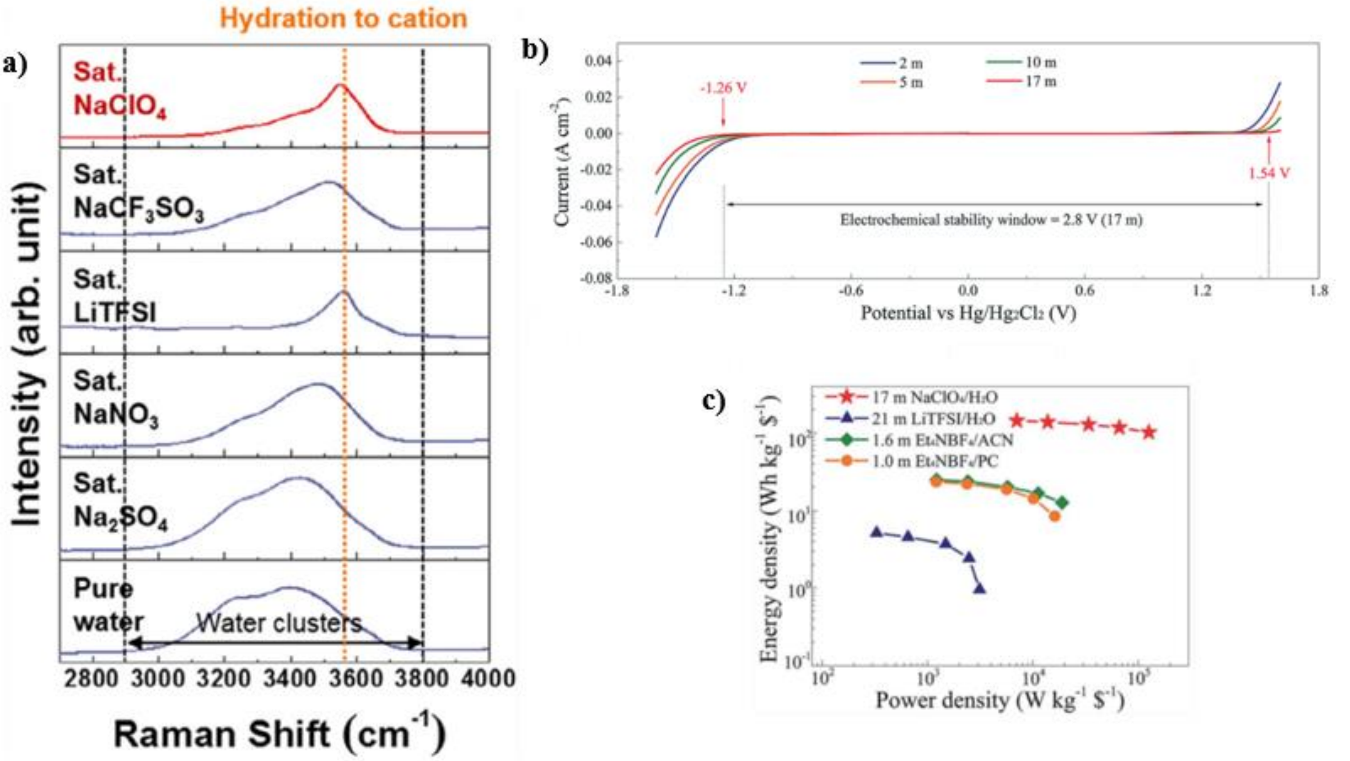

Figure 2. **(a)** Raman spectra of saturated solutions of Na_2SO_4, $NaNO_3$, LiTFSI, $NaCF_3SO_3$ and $NaClO_4$ in water (M. Lee *et al.*, 2019). **(b)** ESW of electrolytes containing different concentrations of $NaClO_4$ and **(c)** Ragone plot normalized by the electrolyte prices (Bu *et al.*, 2019a). The "m" inside the figures means mol kg^{-1}".
Source: Reproduced from M. Lee *et al.* (2019) and Bu *et al.* (2019a) with permission from Elsevier and Royal Society of Chemistry, respectively.

Besides perchlorates, acetates and formates allow producing WISSEs with expressive molal concentrations, much higher than that of 21 mol kg^{-1} achieved with LiTFSI, what at first glance looks like a good option for water-in-salt electrolytes. However, only the potassium acetate and formate are soluble enough to reach the WISE condition, which restrains the application of these WISSEs, for example, in supercapacitors and K-ion batteries. Potassium acetate is allowed to produce 27 mol L^{-1} solutions at room temperature according to the solubility table provided in Handbooks, but concentrations up to 32 mol kg^{-1} is also reported in literature (J. Han *et al.*, 2018). The ESW of this electrolyte can achieve values around 3.2 V (Leonard *et al.*, 2018) and Raman spectrum reveals low-intensity bands between 3000-4000 cm^{-1}, indicating the suppressed water activity (J. Han *et al.*, 2018). Nevertheless, ^1H NMR and DSC of 27 mol kg^{-1} CH_3COOK (Thareja and Kumar, 2021) suggest that acetate anions are less effective H-bond breakers than ClO_4^-, which readily affects the cell voltage. While perchlorate WISSEs allow cell voltages up to 2.7 V in symmetric supercapacitors constructed with N-rGO, acetate-based electrolytes show a depressed cell voltage of 2.0 V (Thareja and Kumar, 2021; Tian *et al.*, 2017) (Fig. 3a), almost equal to diluted electrolytes (Bu *et al.*, 2019a). Unfortunately, WISSEs with potassium formate have not been deeply investigated like acetate WISSEs, but in a single report, the authors claimed to reach 4.0 V of ESW (T. Liu *et al.*, 2019).

It is important to highlight that the anion nature has a strong influence on the cell voltage, which is totally related to how the water molecules are structured in solution. The recent work of Reber *et al.* (2021) described the influence of kosmotropic and chaotropic anions, reporting the unviability of using acetate WISSEs for high voltage applications owing to its kosmotropic characteristic (Fig. 3b). The kosmotropric effect of such anion leads to the water organization in huge clusters, which makes the electrolyte prone to water splitting reactions. Despite the use of chaotropic anions is more suitable to reach high voltage devices, they need to act as a solid-electrolyte interphase (SEI) former to prevent the water reduction process in metal-ion battery (An *et al.*, 2016). Yet even chaotropic salts that can form SEI may not be totally adequate to attain high voltages. Droguet *et al.* (2020) described that SEI formation in LiTFSI WISSEs are not able to protect the electrode of the water reduction, which has several impacts on the capacity fading in LIBs. On the other hand, supercapacitors do not need the presence of this protective layer, making the development of WISSEs for this purpose more focused in strategies to enhance the cell voltage.

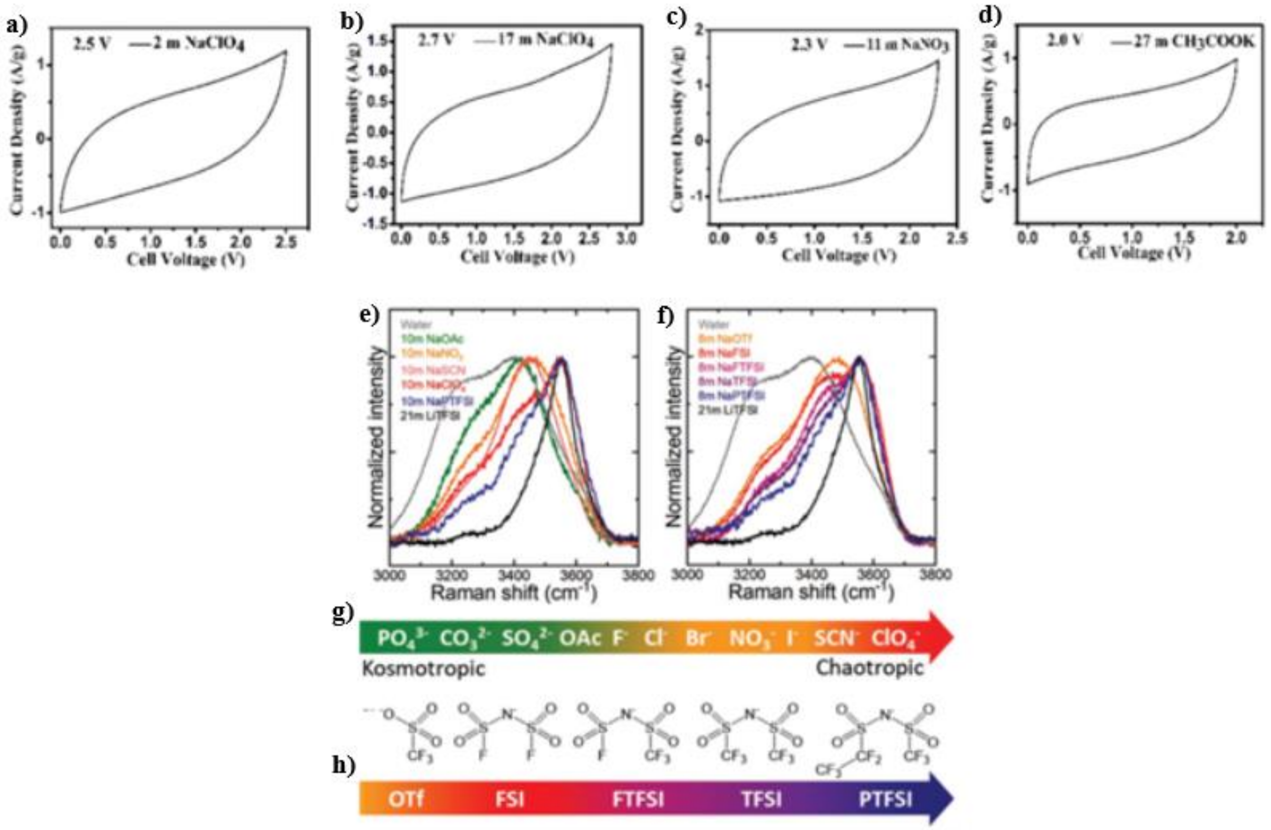

Figure 3. Cyclic voltammograms of symmetric supercapacitors constructed with N-rGO in **(a)** 2 mol kg^{-1} $NaClO_4$; **(b)** 17 mol kg^{-1} $NaClO_4$; **(c)** 11 mol kg^{-1} $NaNO_3$; **(d)** 27 mol kg^{-1} CH_3COOK (Thareja and Kumar, 2021); **(e)** and **(f)** Raman spectra of several WISEs; **(g)** and **(h)** Kosmotropic and chaotropic series of anions in water (Reber *et al.*, 2021). The "m" inside the figures means mol kg^{-1}".

Source: Reproduced from Thareja *et al.* (2021) and Reber *et al.* (2021) with permission from American Chemical Society and WILEY, respectively.

In terms of transition metal salts, only few WISSEs have been reported in literature being $AlCl_3$ (Pan *et al.*, 2019), $Al(ClO_4)_3$ (Zafar *et al.*, 2022a), $ZnCl_2$ (Sun *et al.*, 2022; B. Yang *et al.*, 2022), and $Zn(ClO_4)$ (Zafar *et al.*, 2022b) the only traced out so far. Yet, $AlCl_3$ is not so soluble, and the evidence of low free water content is questionable (Pan *et al.*, 2019), as $NaNO_3$ WISSEs (Guo *et al.*, 2019). On the other hand, $ZnCl_2$ can be used to produce solutions up to 31 mol L^{-1} which makes its WISSE interesting for Zinc batteries. L. Zhang *et al.* (2019) evaluated the effect of $ZnCl_2$ content in the electrolyte, claiming lower capacity fade when 30 mol kg^{-1} is employed instead of 1 mol L^{-1}, depicting capacity retention of 51.1% after 100 cycles at 50 mA g^{-1}. In other work, Wu *et al.* (2019) also employed $ZnCl_2$ WISSE in a dual-ion battery, where the high concentration of salt hinders the ferrocene anode dissolution and shifts the potential of the reactions, as expected by the Nernst equation. Therefore, $ZnCl_2$ WISSEs have a higher concern about increasing the activity of the Zn^{2+} ion in solution than achieving higher ESW. Evidently, the ESW is an important issue for Zn-ion batteries, since the zinc plating in diluted aqueous solution has the inevitable hydrogen evolution reaction (Ma *et al.*, 2020).

Additionally, the aforementioned works do not describe any evidence about the WISE behavior in their electrolytes, which are not so impressive for such applications but allows a better comprehension of water-in-salt electrolytes.

4. Water in bi-salt (WIBSE)

The use of mixed salts in WISE has been proved as a smart approach to overcome the preclusion of low-cost lithium salts that are not soluble enough to reach low water content in the electrolyte. In fact, the addition of lithium might appear only as a strategy to allow the use of low-cost WISE for LIBs, but its implications go further than expected. Lukatskaya *et al.* (2018) were the first researchers to produce, characterize and apply WISEs with two acetate salts. Although the idea of combining two high-soluble salts appeared earlier in the work of Suo *et al.* (2016), who employed mixed LiTFSI+LiOTf salts, the combination of acetates goes further allowing higher capacities for both electrodes. To reach a better composition of the acetates mixture the authors evaluated several ratios of KAc mixed with LiAc and found the formation of a eutectic-like mixture, where the water-to-cation ratio is smaller than that for pure KAc. Similarly, Chen *et al.* (2020a) evaluated several WISSEs based on alkaline acetates, realizing that CsAc can reach higher ESW than that of KAc, due to the higher solubility of the former. Conversely to the upkeep of ESW observed by the Lukatskaya *et al.* (2018), the CsAc+LiAc electrolyte displayed a slight decrease, which is unreasonable because the higher content of salts should produce higher ESW. Lithium-free mixed WISSEs were recently evaluated by J. Han *et al.* (2020b) that also employed acetate salts to prepare the electrolytes. The WIBSE prepared with 32 mol kg^{-1} KAc + 8 mol kg^{-1} NaAc, called 32K8N, attained an ESW of 2.4 V onto stainless steel, which is slightly lower than the one obtained by Lukatskaya and Chen groups. Apart from that, these authors employed Differential Electrochemical Mass Spectrometry (DEMS) to prove the stability of the produced WIBSE. According to their results, no O_2, H_2, and CO_2 evolutions were detected in the potential range of ESW that is an important observation as gas evolution is one of the processes involved in capacity fading. A recent work by Turgeman *et al.* (2022) also demonstrated the feasibility of using WIBSE for Li-ion batteries. The authors developed an electrolyte by mixing LiCl and CsCl salts under high concentrations, which can work stably in a TiO_2|LMO Li-ion battery for up to 1500 cycles.

The water-in-bisalts using low-cost salts are still a new field to be explored and lack of works in literature. To the best of our knowledge, only these three quoted works have been studied the mixed acetates WISE. Interestingly, the concept introduced by Reber *et al.* (2021) of kosmotropism and chaotropism of the ions has a direct relationship on the WIBSE and may be applied for developing new mixed electrolytes. Jenkins and Marcus (1995) described that the nature of the ions can make the solution more viscous or more fluid in comparison with the pure water and designated such behavior as kosmotropic and chaotropic, respectively. For instance, LiAc is well reported as a chaotropic agent used for biological purposes and its behavior in the mixed WISSEs can be interpreted as follows. Although the acetate anion displays a moderate kosmotropic effect, Li^+ is a bit more chaotropic than K^+ (Salis and Ninham, 2014), which can increase the solubility of the species as observed in eutectic phase systems. Similarly, the production of $LiClO_4$+$NaClO_4$ may be interesting to improve the solubility of both species, since the Li^+ displays a higher chaotropic effect compared with that of Na^+ (Rossetto *et al.*, 2008).

Despite the high cost of LiTFSI, the recent work of Xu *et al.* (2022) described the development of a ternary WISE containing LiTFSI-KOH-$CO(NH_2)_2$-H_2O, with lower content of the Li salt (4.5 mol kg^{-1}), which was successfully employed in Li-ion battery. Although the use of eutectic mixtures is not so recent (Lukatskaya *et al.*, 2018), these authors added a non-electrolytic salt to produce its electrolyte that allowed expanding the ESW up to 3.3 V.

5. Redox-active WISEs

Recently, the employment of redox-active species on WISEs has demonstrated a suitable strategy to enhance the energy density of hybrid supercapacitors. J. Park *et al.* (2022) developed a $NaClO_4$ WISE containing bromine and cobaltocene species as positive and negative redox shuttling, respectively. The authors found high power and energy densities for a supercapacitor constructed with single-walled carbon nanotube (SWNT) electrodes and the dual-redox active species. Although the advantage in enhancing the energy storage parameters, the cross-diffusion of the redox species is the main drawback that can lead to a fast self-discharge of the device as proved by the authors. In such case, the use of ion-exchange membranes is suitable to prevent cross-diffusion, but its employment is quite difficult considering the current shape of commercial cells. The use of bromine and iodine salts as redox-active species were also evaluated for micro-supercapacitors (Meng *et al.*, 2022; Wang *et al.*, 2022) and displayed an expressive enhancement of the electrode capacity due to the redox reactions.

6. Is the performance of WISE employed in EES devices competitive?

The current scientific scenario of energy storage devices is a competition for finding the best process or materials that often only care about the final performance. Although the recent developments of low-cost WISEs, much effort is still needed to understand these electrolytes. In terms of WISEs utilization in supercapacitors, which is a simple device, the main advantage is related to widening the cell voltage that allows for achieving high energy densities. In the work of Bu *et al.* (2019a) the sodium perchlorate WISSE allows the carbon-based device to work in a cell voltage of 2.3 V and a specific capacitance about 30 F g^{-1}. Pang *et al.* (2020) subjected a symmetric cell containing $NaClO_4$ WISSE to 2.4 V cell voltage, but the non-triangular shape of the galvanostatic charge-discharge curves suggests a low energy efficiency for their devices. They obtained a specific capacitance of 59 F g^{-1} for such a device, slightly higher than Bu's device, which can be attributed to the Faradaic process evidently present in that work. Comparisons between the obtained specific capacitances with WISSEs are difficult to be done since most of the works employ different electrode materials for constructing their devices. For instance, devices with YP-50F electrodes with sodium perchlorate WISSEs reveal higher specific capacitances than those using LiTFSI (Bu *et al.*, 2019a). Tian *et al.* (2017) attained 69 F g^{-1} for a symmetric device with activated carbon (AC) electrodes and potassium acetate WISE. However, these authors prepared the electrolyte with 75 wt. % of KAc, which is related to a 7.64 mol kg^{-1} concentration and might have a high content of free water. A comparative study of different WISEs reveals (Guo *et al.*, 2019) that capacitance increases in the order 12 mol kg^{-1} $NaNO_3$ > 17 mol kg^{-1} $NaClO_4$> 21 mol kg^{-1} LiTFSI > 27 mol kg^{-1} KAc. Even if the 12 mol kg^{-1} $NaNO_3$ does not display the Raman band characteristic of WISEs, this expressive concentration was able to extend the cell voltage to 2 V. Since the ions in WISEs have a bit different ionic size than that in dilute solutions, it is expected in the future the evaluation of carbon materials with distinct pore size distributions to improve the compatibility among the device components.

Until now, the WIBSEs have not been evaluated for supercapacitor devices, but the difference in the ionic size of the components should be interesting to improve the specific capacitance. Furthermore, much of the commercial devices operate with at least 2.7 V (Yassine and Fabris, 2017), which is slightly higher than the cell voltage commonly utilized for supercapacitors with LC-WISSEs. Also, none of the LiTFSI WISSEs can reach such voltage. Another important issue that is questionable even in most lab-scale devices is the lifespan that commercial supercapacitors have strong retention after more than 500,000 cycles. The work of Bu's group evaluated the constructed supercapacitor at 1 A g^{-1}, and the capacitance loses 20% of its initial value after 10,000 cycles. This retention value is much lower than the required for commercial supercapacitors and none of the works investigated the reason that leads to this fading process. Additionally, the charge storage efficiency is another confusing parameter in supercapacitors that might be carefully evaluated for WISE. The coulombic efficiency is also an important parameter, but to assign it as the energy efficiency the galvanostatic charge-discharge curves need to be a straight line, otherwise, it can overestimate both efficiency and cell voltage. Commercial supercapacitors have high energy efficiencies (Eftekhari, 2017) reaching values close to 100%, but most of the lab-scale devices are far from this value (Laheäär *et al.*, 2015) Although some works display the near triangular shape of galvanostatic charge/discharge (GCD) curves, most of them show deviances from the linear behavior close to the limit of the cell voltage.

For metal-ion batteries, the use of LC-WISE often involves cathodes and anodes that have been previously evaluated in diluted electrolytes, but under this condition exhibit low cyclability. $LiMn_2O_4/TiO_2$ electrodes are known to display battery behavior in $LiSO_4$ electrolytes (S. Liu *et al.*, 2011), but their capacity retention is poor due to water splitting process. Yet, the use of WIBSE of LiAc+KAc allowed the device to operate with a higher cell voltage, however, the cycling tests were performed up to 100 times for the cathode which does not permit ensure the lifetime expansion. In terms of specific capacity, both electrodes of the device depicted similar values to those obtained in an organic electrolyte containing LiPF6, reaching specific capacities around 90 and 120 mAh g^{-1} at 0.1 A g^{-1} for anode and cathode, respectively. Similarly, M. Lee *et al.* (2019) studied the application of $NaClO_4$ WiSSE for Na-ion batteries constructed with $Na_4Fe_3(PO_4)_2(P_2O_7)$ cathode and $NaTi_2(PO_4)_3$ anode, which was also evaluated in diluted aqueous electrolytes (Fernández-Ropero *et al.*, 2018; S. Park *et al.*, 2011). The authors displayed a notable cycle stability for the device when WISSE was employed, improving the capacity retention and coulombic efficiency to 75% and 99%, respectively. Leonard *et al.* (2018) performed a comparative study of potassium acetate WISSE and KPF_6 in an organic electrolyte to evaluate $KTi_2(PO_4)$ anodes, finding better kinetics for the WISSE than that in non-aqueous electrolyte. They also described the formation of SEI consisting of a carbon layer upon the anode material, which may come from the acetate reduction, nevertheless, further studies are still needed to improve the discussion of SEI growth in such electrolytes. Moreover, the electrode was cycled 11k times and displayed 69% capacity retention, a value that is expressive for battery materials. Although LC-WISEs applied to batteries seem to be a good strategy to overcome economical and safety concerns, the energy density and self-discharge for these electrolytes are far from the metal-ion batteries using aprotic solvents (Droguet *et al.*, 2020). Thus, extensive investigations dedicated to comparing electrode materials in typical non-aqueous electrolytes and WISEs are valuable for ensuring the viability of replacing the currently employed electrolytes.

Besides comparing the energy and power densities of devices constructed with WISEs, the self-discharge must be evaluated even more when working with redox-active WISEs that often display cross-over diffusion of active species. In terms of WISSEs for supercapacitors, only few works employing low-cost salts have investigated the self-discharge of such devices and most of them have studied quasi-solid-state electrolytes that exhibits tortuous path for electrical charges diffusion (Deng *et al.*, 2021; Fan *et al.*, 2020; Shi *et al.*, 2022). For conventional liquid electrolytes, Zheng *et al.* (2022) displayed those high concentrated electrolytes based on LiCl and LiBr (14 mol L^{-1}) show suppressed self-discharge when compared with their diluted solutions (1 M) for MXene-based electrodes. Also, when working with metal ion batteries the self-discharge study can clarify the solid electrolyte interface dissolution (Droguet *et al.*, 2020).

7. Perspectives

The use of LC-WISEs is very recent and has a limited number of salts that fits the requirements for preparing them. However, this research field still has a variety of opportunities that can be used to improve the current state-of-art of such electrolytes. Here, we highlight some promising approaches in developing WISEs, exploring from the basics to their final application in energy storage devices.

Initially, the structure of WISEs should be deeply investigated and the boundary conditions to achieve such kind of electrolyte needs to be well defined. Suo *et al.* (2015) described WISEs as a solution where the number of water molecules capable to solvate the ions is far below the solvation number of conventional diluted electrolytes. They described concentrations >5 mol kg^{-1} behaving like a WISE, which is expected for each LiTFSI that exhibits 11 molecules of water. While Li^+ first solvation shell can accommodate 4 water molecules the TFSI- supports an average of 6 molecules at 5 mol kg^{-1} (S. Han, 2018), which is in agreement with WISE definition. Other alkali cations, e.g., Na^+ and K^+ are allowed to support 5-6 water molecules (Luo *et al.*, 2015), a bit more than for Li^+, suggesting that lower salt concentrations can be used to produce WISEs in this case. Nevertheless, anion hydration and the formation of ion pairs should be also considered, but the last may have more importance in concentrated solutions. For instance, $NaClO_4$ diluted solutions may have 6 and 4 (Bergstroem *et al.*, 1991) water in the first hydration sheath of cation and anion, respectively. On average, by considering no ion pair formation the WISE behavior of $NaClO_4$ solutions should be reached in similar concentrations of LiTFSI, around 5 mol kg^{-1}. Yet, Raman spectra of LC-WISE even display a weak response assigned to water clustering that suggests the presence of small content of free water in the solution. Therefore, elucidating the microscopic structure of the WISE solution is needed to improve the comprehension of these electrolytes. Although the algebraic estimate leads to assert about the formation of WISE, even low contents of free water can reflect in high molar concentration of H_2O, which limits the ESW.

Chaotropic salts reveal to be more interesting than kosmotropic ones for WISEs preparations, but the latter has lower costs than the former. The combination of these two kinds of salts should be valuable to reach a better cost/benefit WISE. Differently from the mixture of acetates previously described, the utilization of salts with different anions should be interesting, as demonstrated for W. Lee *et al.* (2018), Sennu *et al.* (2020), Suo *et al.* (2016) and J. Zhu *et al.* (2020). The balance between highly soluble chaotropic and kosmotropic salts should be a strategy to suppress the free water content. Sennu *et al.* (2020) studied mixtures of NaTFSI + NaAc as an approach that allows the extension of the ESW. They claimed that the addition of NaAc to form a WIBSE can neutralize the acidic environment of the NaTFSI WISSE, leading to an electrolyte with improved stability.

Moreover, the investigation of cosolvents acting as additives in WISEs are interesting and has been proved to be effective for enhancing the electrolyte properties. For example, Dou *et al.* (2018) prepared acetonitrile/water-in-salt electrolyte (AWISE) which allowed to achieve the same cell voltage of WISE, but using only 5 mol kg^{-1} LiTFSI. In fact, there are no reports describing the chaotropic effect of acetonitrile in water, but the use of cosolvents also decreases the content of water that is useful because this approach should allow decreasing the amount of salt employed in preparing WISEE. Furthermore, the viscosity and conductivity of AWISE are more adequate for energy storage purposes than in WISE. A similar behavior was observed when with AWISE prepared with $NaClO_4$ (Dou *et al.*, 2019), where the Raman spectra suggest lower free water content compared with this perchlorate WISSE (Bu *et al.*, 2019a) Certainly, the use of acetonitrile displays implications about flammability concerns, but the authors describe that this AWISE is non-flammable under the proposed experimental conditions.

Therefore, there are many promising opportunities unexplored yet that can permit the utilization of these green, low-cost and safe WISEs. Although the great importance in highlighting the performance and improving cell voltage of devices constructed with WISEs, the electrolyte needs to be well studied to allow further rational developments. Viscosity and conductivity measurements of the electrolytes at different concentrations should be conducted since they are important to evaluate the formation of the ion pair. The characterization of the electrolyte by Raman spectroscopy and NMR is needed to understand the chemical environment of the water molecules and also permits comprehending the ionic association. Despite the rapid progress in the field, the necessity of performing such measurements is vital for the development and utilization of new WISEs.

Authors' contribution

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