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Most Modern Supercapacitor Designs Advanced Electrolyte and Interface

Yachao Zhu and Olivier Fontaine

Abstract

Electrolyte plays a key and significant role in supercapacitors. The interaction of an electrode and a chosen electrolyte has a significant effect on the parameters, i.e., ionic conductivity, stable potential range, and charge transfer coefficient, therefore determining the corresponding performance. The captivating interface between electrode and electrolyte is also pushing the intensive research. In this chapter, we focus on two kinds of electrolytes, including water-in-salt electrolytes and redox-ionic liquid. Water-in-salt electrolyte is drawing continuous attention thanks to the formed hydrophobic layer on the positive electrode and solid electrolyte interphase (SEI) on the negative side, preventing water splitting. On the other side, redox-ionic liquid, taking advantage of the broad and stable working window, on the interface, the redox shuttle passes and targets the suitable electrode bulk, leading to redox reactions to highlight capacitance and energy.

Keywords: electrolyte, water-in-salt, redox-ionic liquid, interface, supercapacitor

1. Introduction

Apart from the electrodes [1–4], the essential electrolyte is also one of the most critical components to building the advanced supercapacitor, which involves electrochemical stable voltage window, capacitance, power density, lifetime, stability, and safety [5–7]. According to the calculation of energy, energy density is proportional to the square of the cell voltage, suggesting that it is more influential in enlarging the voltage window, which is decided mainly by the nature of applied electrolytes [8, 9]. As a critical parameter, to match the applied electrode material, the selected electrolyte has a significant impact on the interface between electrode and electrolyte, ionic conductivity, and charge transfer, therefore determining the performance of supercapacitor [10]. As shown in **Figure 1**, the publications number of electrolyte research largely increases over the past decades, signifying its promising research potential. Usually, the electrolyte is composed of salt and solvent. In the light of the classification tree of electrolytes, generally, the electrolyte includes the liquid electrolyte, solid-state or quasi-solid-state electrolyte, and redox-active electrolyte. Liquid electrolyte contains aqueous, non-aqueous, and water-in-salt electrolytes. Redox-active electrolytes include aqueous, ionic liquid, and some gel polymer electrolytes (**Figure 2**).

There into, the highlighted merits of wide working voltage window, adsorbing solid-electrolyte interphase, or enhanced redox moiety earn considerable attention

Figure 1. The statistics of publications of electrodes and electrolytes. Search formulation: (“supercapacitor*” or “electrochemical capacitor*” or “ultracapacitor*” or “double-layer capacitor*” or “pseudocapacitor*”); searched from web of science; search time: 15, Feb 2021.

Figure 2. The classification tree of electrolytes for supercapacitor.

on water-in-salt electrolyte [11] and redox-ionic liquid electrolyte [12]. Despite safe, green, and low-cost, aqueous electrolyte already reaches the ceiling of limited voltage (1.23 V), which impedes the practical applications in high-energy supercapacitor [13–15]. Based on the definition of energy, the working voltage window plays a vital role in boosting the energy. In this regard, except replacing with non-aqueous electrolyte, water-in-salt electrolyte, breaking through the thermodynamic stability limits of water, is prevailing in energy storage [16–20]. As followed main standpoint, for the positive electrode, anions are forced to aggregate at the interface, thus shaping a dense hydrophobic layer to insulate the water from the electrode and further pushing more positive potential. For the negative side, it is agreed that a solid electrolyte interphase (SEI) forms to suppress the hydrogen evolution

reaction (HER), thereby bringing downward more negative potential. It is found that the SEI can block the electronic conduction, but the ions can still pass [21–23]. However, the formation mechanism is still controversial, especially considering the period and the way of decomposing TFSI anions to form SEI, together with water decomposition. Besides, to promote energy, another strategy is to stimulate capacitance. Except scheming new intricate electrode materials, a redox-ionic liquid electrolyte [12, 24–27] leads to an explosion of research in practical applications, such as supercapacitor. Initially, the inert ionic liquid has many good merits, including a wide working voltage window, low vapor pressure, non-flammability, and good thermal stability [28–31]. Building the primary ionic liquid with active redox species can result in an enhanced electric double-layer capacitor, on/near the interface, occurring ions adsorption/desorption, and fast reversible redox reactions [32]. Taking advantage of the wide working window and redox moiety contributions can motivate higher energy for supercapacitor. But it is worth noting that the mechanism is still open in the case of a supercapacitor containing redox shuttles on/near the interface, mainly varying different redox components.

2. Water-in-salt electrolyte

Depended on the malleable potential window, the water-in-salt electrolyte has been extensively reported in numerous papers thanks to SEI's great stability. It is significant to figure out the basic fundamental of SEI formation for further practical applications.

2.1 The concentration effect of water-in-salt electrolyte

Water-in-salt electrolyte, once reported, has been widely researched in lithium-ion batteries and supercapacitor. As shown in **Figure 3**, salt-in-water, exhibits a conventional solvation sheath structure, including a primary solvation sheath and loose-bound secondary solvation sheath. The anion and cation are isolated by water. Compared with the salt-in-water part, the essence of water-in-salt is that the high-soluble-capability salt with extra high concentration (more than 20 m) is dissolved in water, and the insufficient water is not able to neutralize the electrostatic field of Li^+ , thus resulting in anion-containing-cation solvation sheath, where it occurs the corresponding interactions between cation and anion. Initially, a series of concentrated

Figure 3.
 The difference between salt-in-water and water-in-salt electrolytes.

lithium bis(trifluoromethyl)sulfonimide (LiTFSI) electrolytes were first reported by Suo et al. [33] For various concentrations of LiTFSI, cyclic voltammetry (CV) program was used to evaluate the electrochemical stability window, which is depicted in **Figure 4**. On the positive electrode, increasing the concentrations, it displays increasing the concentrations show that the oxygen evolution process is gradually suppressed until having an onset potential of 4.9 V at 21 m (**Figure 4B**). On the positive part, for hydrogen evolution, a passivation process is found as increasing the concentration, which visualizes the plateaus, further pushing the onset potential more downward, namely, from 2.63 V to 1.90 V (**Figure 4A**). Extending the potential operating window is remarkable, compelling to figure out the story on the electrode surface.

2.2 The principles of water-in-salt electrolyte

The story on the electrode surface is captivating to find out in water-in-salt electrolytes. Numerous studies have been conducted to shed light on the mechanism underlying the broadening of the operating voltage window, employing a variety of characterization techniques. First, on the positive surface, although it is almost certain that TFSI anions combine to form a dense hydrophobic layer that separates the water from the electrode, the ions remain mobilizable. The debate mainly focuses on the negative side, where the formation mechanism of solid electrolyte interphase (SEI) is still controversial. The SEI existence efficiently obstructs the water approaching the electrode's surface, but lithium ions still pass quickly,

Figure 4. The electrochemical stability window of LiTFSI-H₂O electrolytes with various molality on nonactive electrodes. (A) and (B) Magnified view of the regions of outlined on negative and positive sides, (C) overall electrochemical stability window. This figure has been adapted from Ref. [33] with permission from Science.

thus suppressing the hydrogen evolution reaction (HER). One of the authentic explanations is from Dubouis et al. [34], as shown in **Figure 5**: initially water is reduced starting from the onset potential, and OH^- is released along with H_2 . Then OH^- bonds with Li^+ to have LiOH , which is deposited on the surface. After that, a nucleophilic attack occurs between LiOH or OH^- and TFSI anions (electrophilic sulfur, precisely), generating F^- and some organic compounds, which bond with Li^+ again to form a fluorinated layer, i.e., SEI. Significantly, the authors demonstrated that the decomposition procedure of water and TFSI is proceeding simultaneously. Bouchal et al. [35] disclosed a precipitation/dissolution model, meaning that the SEI is not stable following continuous dissolution due to local oversaturation at the interface. The calculated model disclosed that the dissolution stems from the driving force, which results from adverse flows between water (from the solution to the electrode) and ions (from the electrode to the solution). This model is versatile to interpret the SEI formation and then the dynamic decomposition/regeneration of SEI layer in a high-concentration electrolyte. Furthermore, they demonstrated that over reducing free water process, the TFSI is chemically decomposed, while chemical and electrochemical degradations of TFSI occur over reducing bound water.

Water-in-salt definition sets the stage for extending the operating voltage window in aqueous electrolytes, which means that a series of advanced electrode materials in water can still work with an organic-electrolyte-like voltage arrange, therefore targeting the high energy density but still keeping safe, green, and low-cost properties. However, some challenge is still there. The critical issue is that it is not passivated enough to protect the whole electrode surface from water at the first cycle, as shown in **Figure 6** [36]. It is found that the passivation is a gradual process,

Figure 5.
 The diagram of SEI formation. This figure has been reprinted from Ref. [34] with permission from Royal Society of Chemistry.

Figure 6.
 Assessment of the SEI stability over time in 20 m LiTFSI. a) Cyclic voltammetry at 50 mV s^{-1} , the 1st (red) and 15th (green) cycles, and one cycle after 1 h OCV. b) the illustration of SEI about its partial dissolution after a resting period (1 h). This figure has been reprinted from Ref. [36] with permission from Royal Society of Chemistry.

which means that it requires many cycles (around 15 cycles) to establish the entire SEI on the surface. Moreover, the SEI is not the stable and self-healing layer, meaning that it can be decomposed during cycling and regenerated over a resting period. Thus, future work should be focused on figuring out these issues.

3. Redox-ionic liquid electrolyte

Electrochemical capacitors include the electric double-layer capacitor (EDLC) and pseudocapacitor. EDLC discovers a fast ions aggregation/separation on the interface, resulting in high power but low energy because of the accessible area limit. Pseudocapacitors can share the reversible and fast redox reaction on/near the interface, leading to enhanced energy and moderate power. It motivates us that constructing a new electrolyte, which includes the ionic liquid and redox species, can offer a wide working voltage window and redox element, thereby improving the energy without compromising the power.

3.1 The neat ionic liquid

As the third group of solvents, ionic liquid, compared with water or organic solvents, prevails to achieve a larger voltage window. Moreover, Ionic liquids have a low melting point of less than 100°C due to their low volatility and nature as molten salts [37]. As an enhanced electrolyte, its property can still be stretched, such as high thermal stability, high ionic conductivity, and extensive liquid temperature range. Depended on the above merits, ionic liquid has been intensively researched in energy-storage applications, for example, battery and supercapacitor [38–46].

3.2 The enhanced redox ionic liquid

Although ionic liquid displays sizable merits as an electrolyte, the capacitance/capacity is still far from the expectation. Recently, a promoted electrolyte, by bringing in redox species, is earning intensive attention because it can obtain additional faradaic reactions to boost the capacitance [47–52]. Then, the extra capacitance from redox-active additives can lead to higher energy density. However, it is noted that the redox-active moiety could result in robust self-discharge, and the redox shuttles may cause the degradation of performance, for instance, low coulombic efficiency [53]. It is inspiring that the above challenges can be relieved by redox ionic liquid, which was first introduced by Rochefort et al. [24] in a supercapacitor, where the redox-active moiety was covalently combined with one of ions in ionic liquid. Based on EMIm NTf₂ base, Ferrocene was merged with imidazolium cation or bis(trifluoromethanesulfonyl)imide anion to synthesize EMIm FcNTf and FcEMIm NTf₂. As depicted in **Figure 7**, the two-electrode cell with EMIm NTf₂ displayed a rectangular shape, implying a classic double-layer capacitive behavior, namely, occurring ions absorption/desorption on the interface. However, with ferrocene species, the redox peaks could be observed in both EMIm FcNTf and FcEMIm NTf₂ electrolytes, which boosted the specific capacitance. Additionally, the Fc-enhanced anion exhibited a strong suppression of self-discharge, resulting in an increase in energy density and stability.

Thanks to the first successful modifying ionic liquid with redox moieties, numerous works have been reported for redox ionic liquid. However, the majority of research has concentrated on integrating a single redox species with a cation or anion, which limits the redox contribution to capacitance. In our team, Fontaine et al. [54] constructed a biredox ionic liquid, as displayed in **Figure 8**, where a

Figure 7.
Cyclic voltammograms based on three ionic liquids. This figure has been reprinted from Ref. [24] with permission from ELSEVIER.

Figure 8.
Structure of BMImTFSI and biredox AQ-PFS⁻ MIm⁺-TEMPO^{*}. (a) Charge storage mechanism based on ionic liquid (b) and biredox ionic liquid (c). This figure has been reprinted from Ref. [54] with permission from Nature.

perfluorosulfonate anion linked with anthraquinone and a methyl imidazolium cation connected with TEMPO. Over the charge-storage process, in pure BMImTFSI, the corresponding ions separated on the interface and access to the available porous carbon surface following the classic double-layer capacitive concept without involving any Faradaic reaction. However, with the bulky size and high viscosity property, the electro-adsorbed or trapped redox AQ-PFS⁻ and MIm⁺-TEMPO^{*} were difficult to through the electrode passage, which could suppress the self-discharge. Thus, the trapped biredox species enhanced the capacitance of a few redox reactions, while the large significant capacitance maintained a stable value over 2000 cycles without obvious degradation. This work, as displayed, sets the stage for constructing a high-energy supercapacitor.

The Biredox ionic liquids are the new paradigm in a supercapacitor, meaning that numerous works are missing to understand the “biredox” mechanism. The central component of understanding the biredox paradigm is a better understanding of electron transfer at the interface, which our team recently proposed [55]. The electrons have to transfer from the electrode to the molecule, then leading to the charge storage in the applied electrolyte. Marcus’s theory meticulously describes the transfer process, but the theory must proceed on an ideal flat electrode, where homogeneous and heterogeneous electron transfer occurs. The reality is that it is more complicated with a non-flat electrode, especially, a porous material, as shown in **Figure 9**. According to Marcus’s theory, kinetics involves two parameters: the reorganization energy represents the required energy to reorganize the solvent as it approaches the molecule, and the coupling parameter represents the interaction between the molecule and the electrode. Depended on the parameters, it is practical to use Marcus’s theory to describe the given case in the pore, where the electrode’s porosity is close to the size of the molecule. But, without a good model and experimental basis, it is difficult to depict the effects on electron transfer from the electrode to the molecule. In a word, the related theory is still blank to show the electron transfer movement in the confined pores.

The trick to incorporating redox-active species into ionic liquid is to increase the energy density without sacrificing other properties, such as power density. Except focusing on the electrode materials or upgrading the techniques, the wondrous works about redox and biredox ionic liquid have been successfully reported to boost the energy density with contributions from additional redox moieties, meantime suppressing the in-house self-discharge. By storing charges in parts of electrolytes, this promoted energy density offers a new route to build the enhanced supercapacitor, but the energy is still unsatisfactory as lithium-ion battery. The classic double-layer capacitor’s limitation remains that capacitance is limited by the available specific surface area. The redox/biredox species can only migrate to the electrode’s accessible surface area, not to the electrode’s bulk volume. This means that the number of redox/biredox moieties within the pores is limited, reducing the contribution of redox reactions. The current works are concentrating on double-layer electrode materials, primarily porous carbon. A possible solution is to expand the electrode materials, such as pseudocapacitive electrodes that are still capable of rapid charging. But the specific surface area has marginal effects on the capacitance performance. Then the redox/biredox parts may access to the entire volume of electrodes. However, new issues may exist. The theoretical work should be more explored, especially the charging mechanism on the interface regarding to redox species. The confinement effect with the redox/biredox molecules in the pores may give us new ways to advance our ionic liquid system. The charge storage mechanism on the interface with redox/biredox ionic liquid electrolyte is still open in the supercapacitor.

Figure 9. Electron transfer on the flat electrode (A) and in microporous media (B). This figure has been reprinted from Ref. [55] with permission from ELSEVIER.

4. Conclusion

In this chapter, two advanced electrolytes are profoundly discussed. First, in aqueous system, to boost the energy density, water-in-salt electrolyte is focused to improve the operating working voltage window thanks to the crafted-capably interphase. For traditional aqueous electrolytes, the limited voltage arrange largely hinders the development of advanced supercapacitor device. In the water-in-salt electrolyte, the water can be blocked by the formed interphase, but the ions still are free to pass through. By breaking through the limit of potential, it is not a problem to achieve high energy in aqueous electrolytes, compared with that in organic electrolytes. However, as discussed above, the formed interphase needs many cycles to passivate on the whole electrode surface, and it is not stable enough to keep the long cycling charge–discharge procedure. Moreover, the formation mechanism of solid electrolyte interphase is still not clear. The debate is still focusing on the detailed way to shape the interphase, suggesting that the more theoretical work are required to construct the whole map. For redox-active ionic liquid electrolyte, it is compelling to enhance the capacitance by introducing the extra redox reaction to store more electrons in the electrolyte instead traditional electrode, and meantime the large voltage window is kept. Furthermore, based on designing the redox-enhanced species, the biredox electrolyte can be also obtained to boost the capacitance via using two couples of redox molecules. With matching with the proper size of porosity, a confinement effect occurs, further having a positive impact on improving the capacitance, and then energy density. The defect is that the more suitable model and theoretical research are required to paint the whole picture about the electron transfer from the electrode to the molecule. More significantly, the basic issue is still the available surface area for electric double-layer electrode materials, which is almost reaching the ceiling of its natural property. The redox molecule can still access to the available surface rather than bulk of the volume. Now, it is interesting to use the pseudocapacitive electrode materials to combine with the redox ionic liquid. But it is important that the pseudocapacitive material has to match with the applied redox ionic liquid to exert the bulk volume of electrode instead of the limited surface.

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Conflict of interest

The authors declare no conflict of interest.

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