Ionic liquid Gel Polymer Electrolytes for Flexible Supercapacitors: Challenges and Prospects

Authors

Rabia Jamil, Debbie S. Silvester*

Affiliation

School of Molecular and Life Sciences, Curtin University, Perth, Western Australia 6845, Australia

*Corresponding author: d.silvester-dean@curtin.edu.au

Abstract

Ionic liquid gel polymer electrolytes (IL-GPEs) have attracted wide interest in the field of electrochemical energy storage devices, particularly for their use in flexible supercapacitors (FSCs). IL-GPEs integrate ionic liquids (ILs) as either a solvent or as a polymerizable unit. They possess several attractive properties including high ionic conductivity, wide operating potential range, good thermal stability, tunable chemical functionalities and self-healing capabilities. In this short review, an overview of IL-GPEs is provided, first describing their classification, fundamental properties, and chemical design, then detailing some of the most recent essential advances in the field along with their limitations.

Keywords

Flexible supercapacitors, gel polymer electrolytes, ionogels, ionic liquids, poly(ionic liquids), polymers.

1. Introduction

Wearable smart systems (e.g. smartwatches, health-monitoring wristbands, sensors, textile-based electronics such as e-textiles and smart textiles) have significantly spurred the development of flexible wearable devices [1]. Furthermore, recent advances in implantable/wearable healthcare devices have resulted in the development of self-sustaining energy storage devices that can harvest/store energy produced by the body through breathing, sweating, arm movement, and chest compression [1, 2]. Supercapacitors (SCs) have been identified as promising candidates in wearable devices due to their long-term stability, high power density, and easy miniaturization. SCs store electric energy via surface charge storage mechanisms [3, 4]. They rely on ion dynamics and physicochemical interactions at the electrolyte/electrode interface that occur during charging and discharging processes. Flexible supercapacitors (FSCs) are suitable for powering wearable electronics due to their light weight, flexibility, comfort when wearing and safety reasons. The notable distinction between regular supercapacitors and flexible supercapacitors is found in the type materials employed as the electrode and the electrolyte, both of which must be flexible for FSCs [5]. The purpose of this article is to discuss the electrolyte material for FSCs, when based on a gelled mixture of ionic liquids with polymers.

Gel polymer electrolytes (GPEs) consist of a conductive liquid phase embedded within a polymer matrix and can be classified into four categories: aqueous gelled electrolytes, non-aqueous gelled electrolytes, ionic liquid-based gelled electrolytes and redox gelled electrolytes [6]. Ionic liquid (IL) gel polymer electrolytes (IL-GPEs) – also sometimes called ionogels – consist of ILs entrapped within a polymer matrix, having both solid-like characteristics and liquid-like diffusive transport properties [4]. IL-GPEs possess characteristics of both aqueous and organic gelled electrolytes, such as high ionic conductivity [7-9] and a wide operating potential range up to 3.5 V [10]. In addition, IL-GPEs offer attractive features including a broad practical temperature range, and the possibility of self-healing, which opens up new possibilities for their use in high-performance and multi-functional FSCs [11-14].

Furthermore, FSC devices using ionogel electrolytes do not require a separator between the two electrodes, potentially lowering the overall device manufacturing costs [15].

The chemical and physical properties of IL-GPEs can be easily altered to allow for their favourable use in supercapacitors, allowing for less packaging constraints (the gels are leak-proof) and improved safety (they are non-flammable and have very low vapor pressure). Ionogels/IL gelled electrolytes can be classified on the basis of their host networks, with the main ones being either silica based, polymer based or hybrid organic-inorganic based [6, 16]. Among them, polymer-based IL gelled electrolytes have been frequently employed in FSCs. Commonly used polymers include: poly(vinyl alcohol) (PVA), poly(methyl methacrylate) (PMMA), poly(acrylic acid) (PAA), poly(ethylene oxide) (PEO), polyacrylonitrile (PAN), poly(ethylene glycol) blending polyacrylonitrile (PAN-*b*-PEG-*b*-PAN), poly(vinylidene fluoride) (PVDF) and poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-*co*-HFP) [1] (see Figure 1a for some of their chemical structures). Nowadays, there is a variety of research devoted to the synthesis and characterisation of ionogels, summarized in several excellent review articles [1, 4, 17-22]. The chemical structures of some common IL cations and anions that have been used in IL-GPEs for FSCs are shown in Figure 1b.

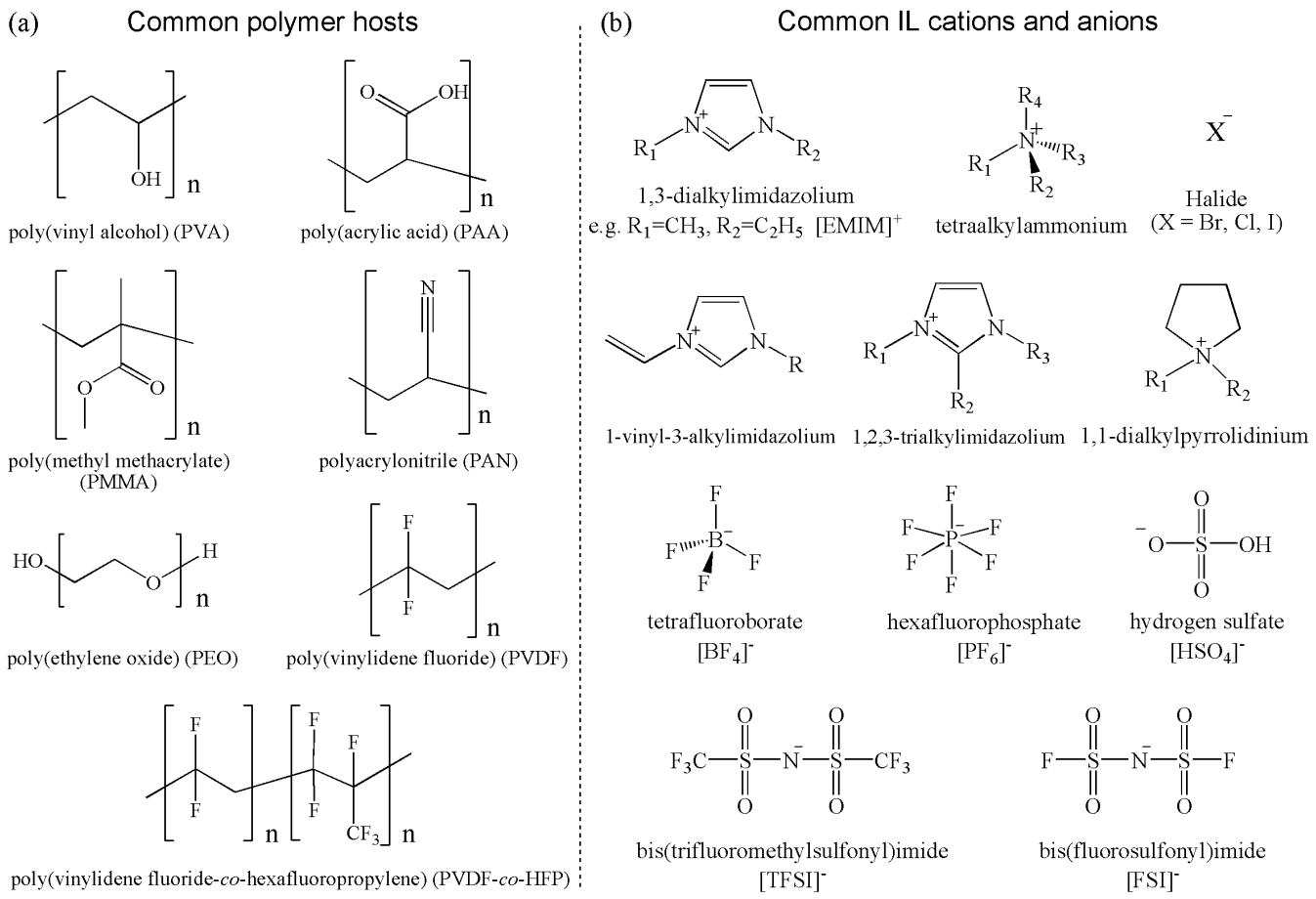

Figure 1. Chemical structures of: (a) polymers, and (b) IL cations and anions, that have been used to construct IL-GPEs for flexible supercapacitors.

This mini-review paper aims to describe some new advances and emerging applications of IL-GPEs used as electrolytes in FSCs over the past three years. It includes a critical discussion on some illuminating improvements to the key performance parameters, and design strategies of IL-GPEs that are targeted towards FSC applications. The aim is to inspire further research in this important area.

2. Ionogels/IL-GPEs in Flexible Supercapacitors

Composition and tuning of IL-GPE electrolytes

IL-GPEs composed of imidazolium-based cations have been extensively investigated for FSCs due to their high conductivity and low viscosity. Low viscosity ILs with small-sized imidazolium cations (e.g. $[EMIM]^+$) embedded into GPEs improves both the specific capacitance and specific energy of the device.[20] A further way to improve the ionic conductivity of imidazolium-based GPEs is to incorporate

boron sites that trap anions. Boron atoms with empty p-orbitals can behave as an acidic center, interacting with the anion of the electrolyte salt to promote cation-anion pair dissociation and, as a result, improved ionic conductivity [19]. IL-GPEs consisting of pyrrolidinium-based cations have been shown to exhibit outstanding electrochemical performance at both room temperature and high temperatures [6]. As a result of their superior cyclic performance and thermal stability, they could have a promising future in high-temperature FSC devices. Other cations, such as short-chained fatty quaternary ammonium salts, offer a wide voltage window, high conductivity, and good stability over a wide temperature range, hence can overcome the safety and stability concerns of FSC devices at high temperatures. Tuning of the IL *anions* also has a strong impact on the physiochemical and electrochemical properties of ionogels [23]. IL-GPEs with inorganic salts incorporated into their structure also give rise to ionogels with increased ionic conductivity and higher electrochemical stability window. The active engagement of both ions from the inorganic salt allows for rapid charge transfer between the electrolyte and the electrode [13, 14].

Intermolecular interactions between IL components and the polymer can regulate the mechanical and electrical properties of ionogels. Aside from the IL composition, the amount of IL in the mixture is also essential; ionic conductivity typically increases as the amount of IL increases, however, it has a negative impact on the mechanical strength [17]. ILs that interact strongly with the polymer matrix are preferred, resulting in increased strength and puncture resistance. The key issue for IL-GPEs in flexible devices is to improve the mechanical strength while preserving good electrochemical characteristics [24]. The use of linear polymers to mobilize ILs should be avoided because they usually have poor mechanical properties, including both low flexibility and strength [15]. The utilization of porous matrices, however, poses a risk of long-term stability due to IL leaching over time. Therefore, strategies for the in-situ entrapment of the IL during polymerization and crosslinking of the polymer, rather than post-polymerization, should be investigated.

The nature of the electrode/electrolyte interface is essential for FSCs [25]. IL-GPEs have been commonly used as electrolytes in supercapacitors in conjunction with carbonaceous materials as

electrodes [26-28]. Carbon materials combined with SIFSIX-3-Ni (an activated carbon-nickel metal organic framework composite) further improves the electrochemical properties of the device when used with an electrolyte such as an IL-GPE [29]. A few investigations demonstrate the use of protic IL or aprotic IL gel-based electrolytes to increase energy storage using metal oxides as electrodes [30-32]. Interfacial interactions between the electrode and the electrolyte, particularly in FSCs working under deformation, should be considered when selecting electrodes for IL-GPEs, because weak interactions lead to fragility upon elongation, and also lead to low power density due to the low surface utilization of the electrode [33].

Ionogel synthesis

IL-GPEs are usually prepared using two main methods: doping and polymerization. Doping methods include solution-casting methods (e.g. by mixing with solvents) and impregnation methods (e.g swelling the polymer with the IL). However, both methods provide little control over the polymer composition. Direct polymerization of monomers dissolved in ILs, on the other hand, is a favorable strategy that eliminates the need for additional solvents and provides a far greater control over the composition, allowing for the design of ionogels with minimal by-products [17].

Crosslinking techniques have been developed in recent years to achieve supported IL-based flexible polymer electrolytes [15]. Watanabe and co-workers first prepared chemically crosslinked ionogels by the in-situ radical polymerization of vinyl monomers in ILs in the presence of a chemical crosslinker [34]. Current materials, however, are often inert or are doped with salts of high viscosity ionic liquids (e.g. those with large ions), and the choice of polymers is frequently limited by the miscibility of specific polymers in ILs, particularly at high degrees of polymerisation. In addition, due to the lack of a recoverable energy-dissipating mechanism during deformation, typical covalent crosslinked ionogels have low mechanical strength and poor recoverability/healable properties [24]. It has been demonstrated that the self-healing ability of IL-GPEs significantly increases the reliability of related SCs [35]. For example, Wu et al. synthesized a diol-borate ester-cross-linked polyvinyl alcohol (PVA) ionogel (PBE90)

electrolyte-based smart FSC with healable features [35]. PBE90 exhibited an amorphous nature with exceptional flexibility, excellent self-healing efficiency of up to 95 % within 30 minutes, and high ionic conductivity due to the dynamically reversible B-PVA cross-linking nature and the effective plasticization provided by the IL, as demonstrated in Figure 2. Similarly, the supercapacitor exhibited excellent resistance to mechanical deformation and could be healed without the use of an external stimulus while retaining most of its electrochemical performance [35]. It is clear that there is a need to develop reversibly highly stretchable multifunctional IL-GPEs that are easily recoverable/healable from fatigue damage and fracture.

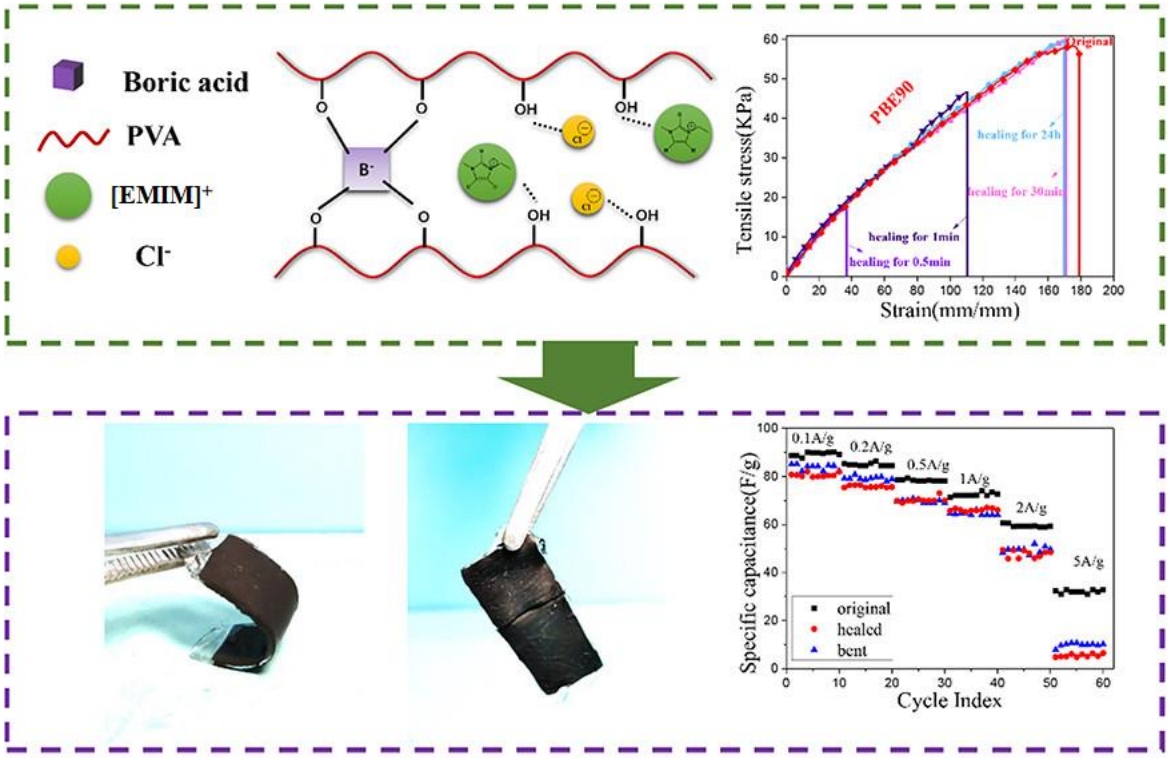

Figure 2: Schematic illustration of a boronic ester cross-linker and the IL distribution in a PVA-BA/[EMIM]Cl ionogel (PBE90) with stress−strain curves of PBE90 after healing for various periods of time (top); From the original form, bending and healing of PBE90-based FSC and cycle life of the original, healed, and bent PBE90-based FSC at 2 A/g. (bottom). Figure was reprinted with permission from reference [35].Copyright 2020 American Chemical Society.

Aside from the different types of ionogels that are available, it is also important to fabricate IL-GPEs onto a substrate using a facile solution technique if they are to be fabricated on a large scale for supercapacitor applications. A poly(dimethylsiloxane) (PDMS) stamp approach provides a reasonable means to prepare such mechanically stable materials [14]. In contrast to other solution-based procedures,

mechanically thin films with a bicontinuous IL-GPE structure can be manufactured for FSCs with a long operating reliability [14]. Figure 3 shows a comparison of the PDMS stamp approach and the spin-coating method, with the former producing IL-GPE films with outstanding structural stability and smooth surface roughness without macroscopic phase separation. SCs with two IL-GPE coating-activated carbon electrodes demonstrated remarkable energy and power densities (44 W h/kg at 875 W/kg and 28 kW/kg at 3 W h/kg, respectively), as well as a dramatic (more than 50%) reduction in current resistance (*iR*) drop, even after mechanical deformation [14].

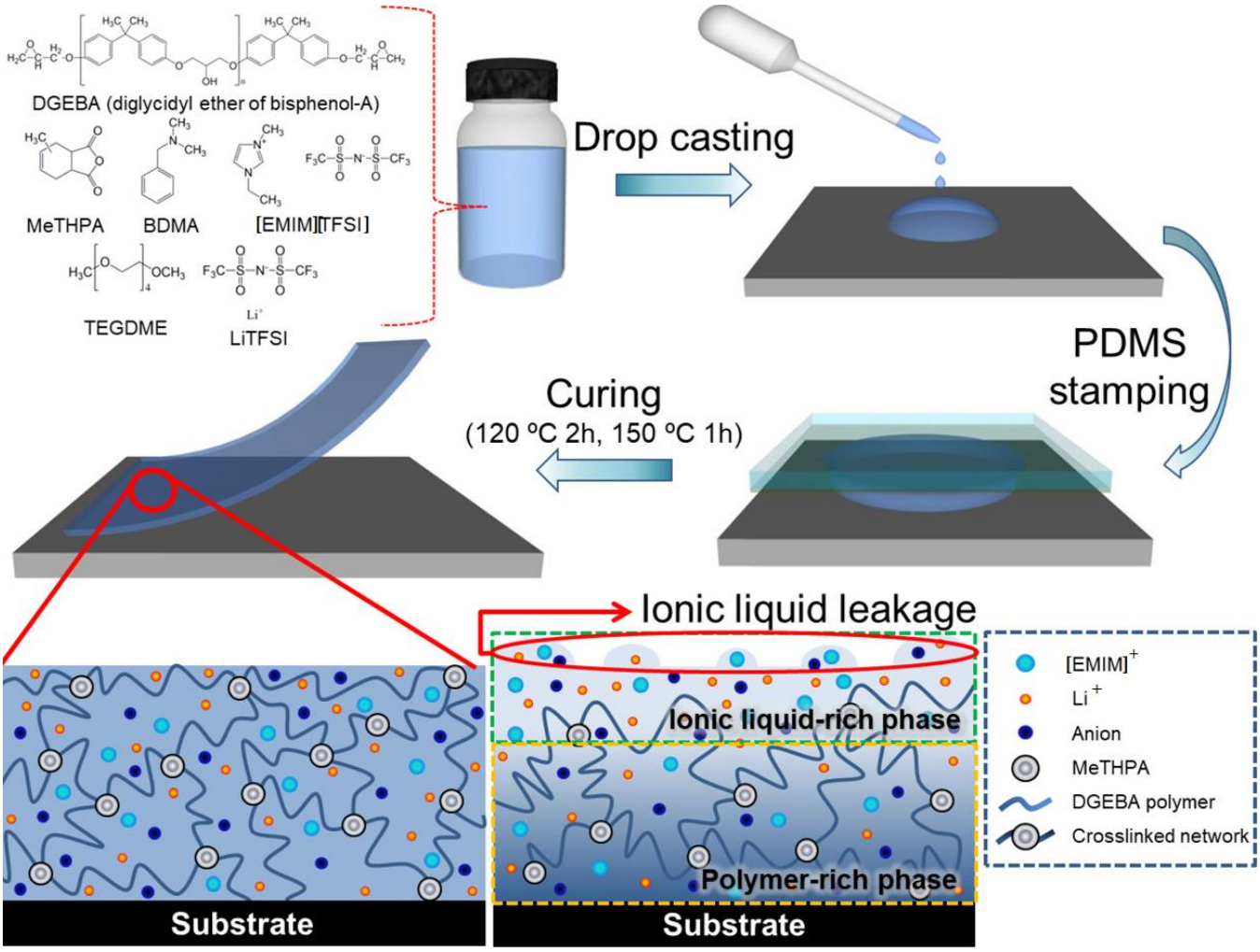

Figure 3. Schematic diagram illustrating the fabrication of a flexible IL-GPE film using a solution-based process via a silicone elastomer stamping method (bottom left - bicontinuous without phase separation), compared to the spin-coating method (bottom right - macroscopic phase separation). Top left: Chemical structures of the DGEBA epoxy resin, methyltetrahydropthalic anhydride (MeTHPA) curing agent, N-benzyldimethyl-amine (BDMA) catalyst, G4 (or tetraglymethylene glycol dimethyl ether (TEGDME)) plasticizer, [EMIM][TFSI] ionic liquid, and LiTFSI salt. The figure was reprinted with permission from reference [14]. Copyright 2020 American Chemical Society.

Poly(IL)/IL binary polymer electrolytes

Polymeric ionic liquids (poly(ILs)) are conductive ionic polymers that contain IL based cations or anions, where one ion is attached to a polymeric chain while the counter-ion is free to move and contribute favourably towards the ionic conductivity [36-38]. Due to their high thermal and electrochemical stability, as well as their miscibility and compatibility with ILs because of their similar structures, poly(ILs) have recently been used as components of both the electrodes (when mixed with graphene) and electrolytes in the production of supercapacitors [39-41]. To address the low ionic conductivity of pure poly(ILs), poly(IL)/IL binary mixtures have been developed in which the mechanical properties of the host polymer co-exist with the electrochemical properties of the ionic liquid [6]. Here, the polymer scaffold acts as a physical barrier between the electrodes, avoiding short circuits, while the entrapped IL removes the danger of leakage, but also provides conductivity [15]. For example, Alexandre et al. used a mixture of poly(1-vinyl-3-propylimidazolium bis(fluorosulfonyl)imide) (poly(VPIFSI)) and the IL [EMIM][FSI] (1-ethyl-3-methyl imidazolium bis(fluorosulfonyl)imide) in a mass ratio of 50:50 as a poly(IL)/IL gel polymer electrolyte which had an ionic conductivity of up to 3.7 mS cm^{-1} [40]. The amount of ionic liquid in the electrolyte should ideally be as high as feasible, because ionic conductivity increases with the number of free ions in the electrolyte [6, 42] The FSC device with poly(VPIFSI)/[EMIM][FSI] gelled electrolyte demonstrated good cyclic stability by retaining 80 % of its capacitance after 5,000 cycles.

Redox active IL-GPEs

IL-GPEs based on ionic liquids are often employed as ionic mediators for charge storage in FSCs. However, it is challenging to increase the specific capacitance of FSCs by using IL-GPEs [6]. A new direction is to use a redox electrolyte, where redox-active materials undergo electron transfer reactions that introduce increased pseudocapacitance, while the electrolyte provides a wide voltage window and outstanding mechanical strength, hence boosting the total specific capacitance and energy density of the device [43].

During charging in an inert electrolyte containing a Br^-/Br_3^- or I^-/I_3^- redox couple, Br^- or I^- ions are attracted towards the positive electrode and become oxidized at the electrode/electrolyte interface. After charging, however, oxidized species self-diffuse towards the negative electrode and are reduced; this process is referred to as self-discharge. The major problem with redox-active electrolytes is the faster self-discharge processes which causes fading in the voltage of the device and energy loss. Compared to traditional inert electrolytes with dissolved redox-active materials (e.g. KOH with KI in water), redox gelled electrolytes with IL additives alleviates the problem of fast self-discharge. In some circumstances, adding carbon nanotubes (CNTs) to a redox ionogel electrolyte not only provides a transport channel to increase the ionic conductivity, but also suppresses self-discharge by adsorbing oxidized ions and preventing their self-diffusion to the negative electrode [44, 45]. Recently, Yadav et al. reported the use of hydroquinone as a redox active material in an IL-GPE, which widened the voltage window (~2.6 V) and improved the capacitive ability of the device (specific energy 24.3 Wh kg^{-1} and specific capacitance 485 F g^{-1}) compared to the electrolyte without hydroquinone (Figure 4) [46].

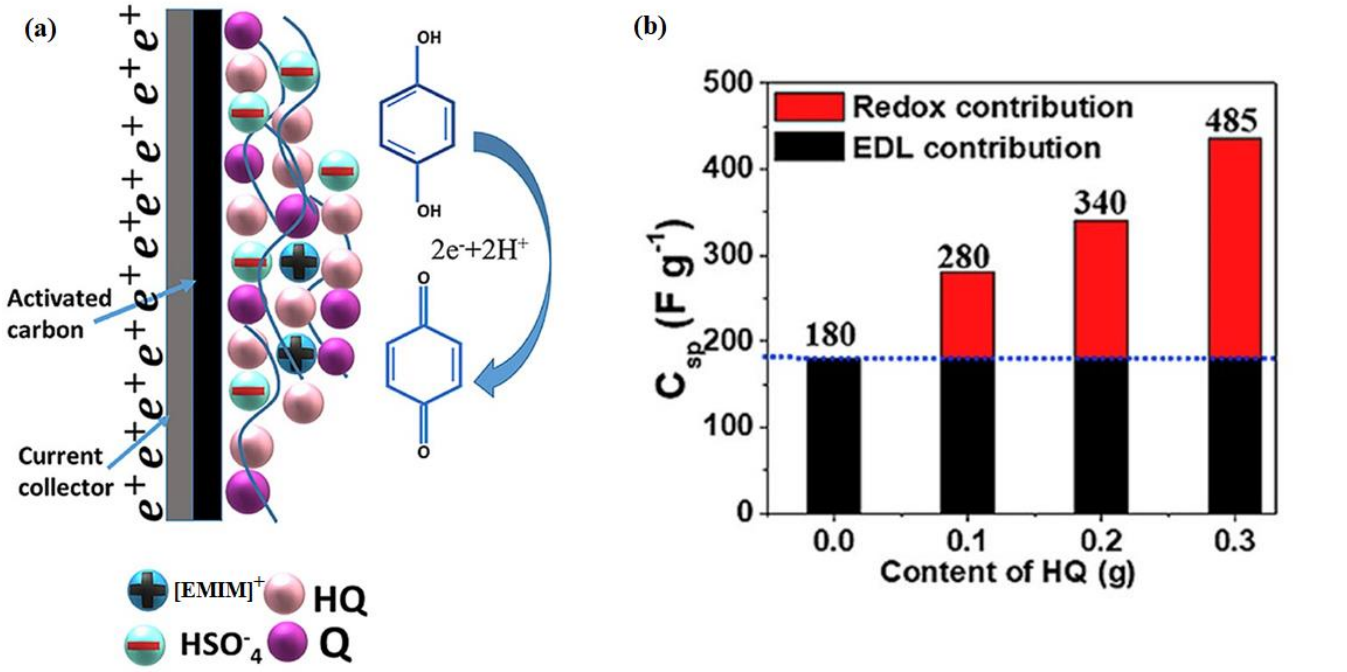

Figure 4. (a) Schematic representation of charging of an electrode in an electrolyte containing a redox additive (HQ = hydroquinone, Q = quinone) in PVA/PVP/[EMIM][HSO_4] ([EMIM][HSO_4] = 1-ethyl-3-methyl-imidazolium hydrogen sulphate). (b) Specific capacitance of the capacitor cell (C_{sp}) with GPEs containing different amounts of redox additive (HQ) at a current density of 0.84 A g^{-1} (contribution of redox process). Reproduced and modified with permission from reference [46].

3. Conclusions

In this mini-review, we have outlined representative utilizations of several IL-based GPEs for flexible supercapacitors over the last 3 years. IL-GPEs afford interfacial charge accumulation across wide electrochemical stability windows – which is important for high energy storage – as well as better stability and cyclic performance. Understanding the ramifications of selecting a certain IL for a given gel scaffold material is crucial when exploring new ILs for ionogel applications. Therefore, the development of IL-GPEs with outstanding performance is a critical step towards the industrialization of ionic liquid FSC electrolytes.

One important factor to consider is the temperature range the device can work under, because they may need to survive the harsh conditions necessary for specialized applications, such as space hardware, oil drilling, high temperature manufacturing processes, etc. [16, 47-49]. It should be noted that when the temperature exceeds the sol–gel transition temperature, the gelled electrolytes can no longer function independently as a separator between two electrodes. This imposes a severe temperature restriction to any device constructed without additional mechanical separation, while also generating additional safety issues about devices functioning during accidental overheating which can cause fires. With this in mind, effective fabrication methods for gelled electrolytes that can maintain physical and electrochemical stability at high temperatures should be investigated. Furthermore, most investigations on self-discharge suppression are carried out at room temperature. Understanding self-discharge mechanisms at high temperatures and investigating efficient suppression strategies are critical for improving supercapacitor applications, and we believe this is one of the biggest challenges going forward.

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Declarations of interest

None

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