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# Ionic Liquid for High Voltage Supercapacitor

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Jeeyoung Yoo

Additional information is available at the end of the chapter

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## Abstract

Pure ionic liquids (ILs) and IL mixtures in organic solvents have been investigated for higher operating voltages around 3.0–4.0 V. ILs have design flexibility due to the numerous possible combinations of anions and cations. Current research on ILs as electrolytes has focused on several ILs, including imidazolium and pyrrolidinium. At early stages, various ILs have been studied as salts of electrolyte with organic solvents like acetonitrile and propylene carbonate. Neat ILs have been applied for high-performance electrolyte, and some of them have been used as electrolyte (1-ethyl 3-methylimidazolium tetrafluoroborate). These liquid electrolytes need additional encapsulation; therefore, SCs applied ILs face difficulty in integration and manufacturing flexible devices. These drawbacks can be solved by adopting a polymer electrolyte because the ILs maintain the conductivity even when solidified, unlike a typical organic electrolyte. Common polymer matrixes such as PVdF, PMMA, and PVA have been suggested to embed ILs. Poly(ionic liquid) (PIL) is also studied. PIL is a polymer electrolyte containing a polymer backbone and an IL species in the monomer repeat unit. PIL-based polymer electrolytes have high ionic conductivity, wide electrochemical windows, and high thermal stability.

**Keywords:** ionic liquid, ion gel, poly (ionic liquid), high voltage supercapacitor, all-solid supercapacitor

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## 1. Introduction

As new markets using energy storage devices increase, various types of energy storage devices are striving to enter the market [1, 2]. In the case of electric vehicles (EVs), Li ion batteries (LIBs), fuel cells (FCs), and supercapacitors (SCs) are in a competitive relationship [3]. LIBs are emerging as the most promising candidates because of their high energy density and technical maturity. However, there is a problem of safety. The unstable supply and price of lithium and cobalt are also serious problems. In addition, FCs still have difficulties in

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commercialization due to the disadvantage of obtaining hydrogen from petrochemistry and the reluctance of establishing a hydrogen station. As an alternative to this situation, SCs can be proposed. Up to now, SCs have been applied to an electric bus using regenerative break and electric train powered by pulse power, since the large power density of SCs is suitable for intermittent power supply [4]. However, SCs are facing with critical challenge of low energy density. Therefore, LIBs and SCs are applied together for the complementary purpose. The operating voltage of LIBs is from 3.5 to 4.0 V and that of SCs is approximately under 2.8 V. If SCs achieve the 3.5–4.0 V rated voltage with high energy densities or LIBs achieve high power densities, then the power supply unit can be minimized and integrated [5]. In other words, if SCs archive high energy density without sacrificing power density, SCs can be applied as an alternative energy storage system replacing LIBs and FCs.

There are two ways to increase the energy density of SCs. One is to enhance capacitance, and the other is to increase the operating voltages, since the energy density is proportional to capacitance and operating voltage. At the initial stage, many researchers focused on widening the electrode area for enhancing electric double layer (EDL) capacitance. Various types of activated carbon (AC) are commercialized as a result of these efforts. Carbon nanomaterials like carbon nanotubes (CNTs) and graphene are also highlighted as large capacitance materials [6]. Additionally, redox active electrode materials like metal oxide and conductive polymer are proposed to enlarge capacitance by pseudocapacitance. However, those materials struggle with process abilities, limiting of electrolyte adoption, charging/discharging properties, minimizing high cost, and checking suitability for commercial production lines. Another approach of redox active materials is electrolyte that contains redox active couples. Representative redox couples are halides, vanadium complexes, copper salts, hydroquinone, methylene blue, indigo carmine, p-phenylenediamine, m-phenylenediamine, lignosulfonates, and sulfonated polyaniline [7]. Most of electrolyte adopting redox couple has a problem of solvent selection because such redox couples are effective in aqueous medium. This means that the operating voltage of aqueous electrolyte containing redox active couple is limited under 1.23 V, which is the electrolysis voltage of water. Such boundaries with electrode materials motivate the development of advanced electrolyte with high operating voltages for high energy densities because the operating voltages for SCs depend on the electrochemical stability window of the electrolyte.

At early stages, classical salts and systems are suggested. The solvent is organic solvents such as acetonitrile (AN) and propylene carbonate (PC) [8]. Quaternary ammonium salts and AN are representative electrolyte of SCs, and their operating voltage is about 2.8 V. The electrolytes adopting AN exhibit large specific capacitance due to high ionic conductivity derived from low viscosity of AN. However, SCs applied AN-based electrolyte have to be operated under 80°C due to the boiling point of AN. Otherwise, PC is less toxic and has higher thermal stability than AN. Thus, the electrolyte adopting PC is generally considered a safe electrolyte. Using PC-based electrolytes can achieve slightly higher operating voltages for SCs than those using AN. However, formation of carbonate and evolution of H<sub>2</sub> and CO<sub>2</sub> caused by reaction of carbon electrode and PC have been identified as the main causes of performance degradation at high voltages [9]. To overcome these drawbacks, many electrolytes have been proposed over the past several years as an alternative electrolyte to increase the

operating voltage of SCs. Next alternative organic solvent for high operating voltage is linear sulfones, alkylated cyclic carbonate, and adiponitrile [10–12]. These alternative electrolytes archive 3–3.2 V of operating voltage. Meanwhile they show relatively high viscosity and low ionic conductivity, these characteristic occur decrement of power density. Another type of alternative electrolyte is the LIBs electrolyte system. These electrolytes contain common solvents (cyclic carbonate for high dielectric constant and linear carbonate for low viscosity) and lithium salts like  $\text{LiPF}_6$ . These electrolytes exhibit high ionic conductivity and high operating voltage over 3 V. However, they have some issues of moisture sensitivity (formation of HF from  $\text{LiPF}_6$ ), slow intercalation reaction of Li cation, and the presence of a solid electrolyte interphase (SEI). These problems are directly connected to electrical performance and safety of SCs. Also, organic solvent is highly flammable and thermally unstable.

To solve these issues, ionic liquids (ILs) are investigated. ILs are thermally stable because they have negligible vapor pressure and they are nonflammable and relatively high ionic conductivity. More importantly, ILs are very effective for widening the operating voltage due to their wide electrochemical stability window over 3 V. Additionally, ILs are composed of only ions, which means that ILs play a role in both salts and solvents. Therefore, there are no additional salts or solvents. For these reasons, ILs have been widely investigated as an electrolyte material.

## 2. Ionic liquid as liquid electrolyte for supercapacitors

### 2.1. Neat ionic liquid as liquid electrolyte for electric double layer

In 1807, Humphry Davy pioneered the study for the electrolysis of molten salts which is referred as ILs later and presented the electrochemical theory of the molten electrolyte, despite the research was concentrated on reactive metal preparation [13]. After that, synthetic method of aluminum with electrolysis of aluminum oxide dissolved in cryolite was suggested by Hall [14]. This method is meaningful that eutectic molten salts were formed at low temperature with electrolysis, and this method is still applied in aluminum industrial production.

ILs have been studied for electrochemical devices such as SCs, FCs, rechargeable batteries, photovoltaic cell, and actuator etc. due to the mobility and flexibility of ions [5, 14–20]. ILs are composed of large and asymmetrical organic cation and charge delocalized inorganic/organic anion by weak interaction [21]. Despite that ILs exist in the cation-anion state, these structures lower the tendency to crystallize, so they provide a fluid phase with reasonable ion conductivity, and they show no decomposition or significant vapor pressure [21, 22]. As mentioned, ILs are composed of organic ions and can be combined to various structures with easy preparation. Thus, various kinds of ILs can be used for the given application with desired properties (**Figure 1**).

Wide tunability of ILs can be combined to satisfy the desired characteristics of SCs such as working voltage, operating temperature range, and internal resistances [23]. For these reasons, ILs have been widely investigated as electrolyte material. As mentioned above, quaternary

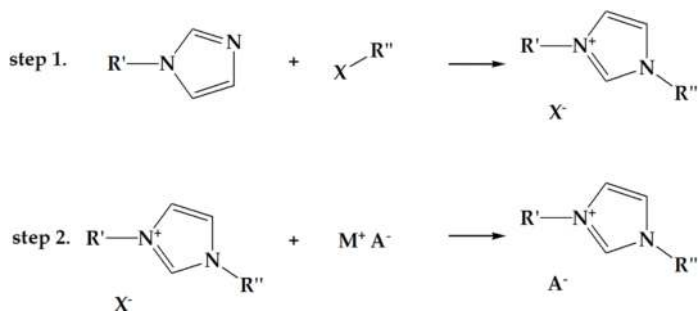
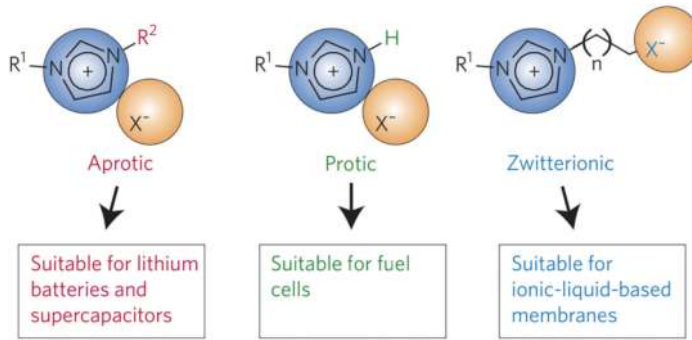


Figure 1. Synthetic mechanism of imidazolium-based ILs.

ammonium salts which is one of ILs are widely investigated with organic solvents, and some of them were already commercialized (1 M of tetraethylammonium tetrafluoroborate ( $[\text{Et}_4\text{N}][\text{BF}_4]$ ) in AN or PC) [24]. Ammonium with different alkyl groups ( $[\text{Et}_4\text{N}]$ , tetrapropylene ammonium ( $[\text{Pr}_4\text{N}]$ ), and tetrabutyl ammonium ( $[\text{Bu}_4\text{N}]$ )) and various anions ( $[\text{BF}_4^-]$ , hexafluorophosphate ( $[\text{PF}_6^-]$ ), perchlorate ( $[\text{ClO}_4^-]$ ), and triplate ( $[\text{CF}_3\text{SO}_3^-]$ ) was applied in organic solvents such as PC, AN,  $\gamma$ -butyrolactone (GBL), and *N,N*-dimethylformamide (DMF). The ionic conductivities generally decrease in the following order:  $[\text{Et}_4\text{N}] > [\text{Pr}_4\text{N}] > [\text{Bu}_4\text{N}] > [\text{Me}_4\text{N}]$ ,  $[\text{BF}_4] > [\text{PF}_6] > [\text{ClO}_4] > [\text{CF}_3\text{SO}_3]$ . Similarly, nonaqueous electrolyte with various alkyl imidazolium salts was studied [25]. According to development of organic electrolyte, carbon electrode material which is effective for enhancing EDL capacitance was investigated. These studies were focused about suitability between the ion size of ammonium salts and the pore size of carbon electrode [26].

ILs can be classified as aprotic, protic, and zwitterionic types. Aprotic type ILs have been used for SCs [21]. In the published literature so far, most of ILs used in SCs are based on imidazolium, pyrrolidinium, ammonium, sulfonium, and phosphonium cations. Anions of ILs are  $[\text{BF}_4]$ ,  $[\text{PF}_6]$ , bis(trifluoromethanesulfonyl)imide ([TFSI]), bis(fluorosulfonyl)imide ([FSI]), and dicyanamide ([DCA]). Among them, imidazolium and pyrrolidinium based ILs were widely investigated because of relatively lower viscosity and reasonable ionic conductivity [27]. Generally, imidazolium salts were used for high ionic conductivity, and pyrrolidinium salts were applied for wide electrochemical stability window [28, 29] (Figure 2). Table 1 shows representative ILs for electrolyte of SCs.

Most ILs in Table 1 have several problems, such as high viscosity, low ionic conductivity, and high cost comparison to typical SCs electrolytes. These issues prevent actual application in SCs. (Numerous ILs maintain solid phase at room temperature.) 1-ethyl-3-methyl imidazolium ( $[\text{EMI}][\text{BF}_4]$ ) shows high ionic conductivity among ILs; however, the ionic conductivity value of  $[\text{EMI}][\text{BF}_4]$  is 23% level in comparison to 1 M  $[\text{Et}_4\text{N}][\text{BF}_4]$  in AN. The viscosity of  $[\text{EMI}][\text{BF}_4]$  is also 130 times higher than common organic electrolyte of SCs [29]. Generally, low ionic conductivity and high viscosity of electrolyte occur increment of internal resistance (equivalent series resistance, ESR) and limit both the energy density and the power density. The energy density is decreased due to Ohmic drop and the power density is also reduced because the power density was oppositely proportional to ESR described as Eq. 1.  $P$  is power density, and  $V$  is working voltage [30].



**Figure 2.** Basic types of ionic liquids: Aprotic, protic, and zwitterionic types [21].

$$P = \frac{V^2}{4 \times ESR} \quad (1)$$

This problem appears to be more severe at room and low temperatures, as evidenced by comparative studies between organic electrolytes and IL electrolytes [22, 28, 31]. These issues are more serious below room temperature. In addition, the EDL capacitance values of ILs adopting SCs can be decreased especially at high scan rates or high charging/discharging rates [32]. Despite these problems, ILs are still attractive materials for electrolytes. ILs show wide stability windows because the ILs are composed of individual ions, which do not participate in any considerable electrochemical reaction over a wide range of potential. Additionally, properties of ILs derived from ionic structure, such as high viscosity, increase the electrochemical decomposition voltage (**Figure 3**).

In terms of the energy density, increment of the operating voltage is advantageous rather than increase the capacitance. The energy density of the SCs is proportional to the square of the voltage as shown in Eq. 2, and E and C are energy density and specific capacitance of SCs, respectively [34].

$$E = \frac{1}{2} C V^2 \quad (2)$$

**Figure 4** shows the energy density difference of typical electrolytes of SCs such as KOH aqueous solution, battery electrolyte, and ILs [35]. The hierarchical carbon nanostructure with mesoporous carbon CMK-5 intercalated between reduced graphene oxide (RGO) sheets was proposed as electrode in this research. According to cyclo-voltammograms, capacitive behaviors of applied electrolyte are very similar; however, the differences of stable windows result in significant differences of energy density. When adopting [EMI][BF<sub>4</sub>], energy density was increased to 60.7 Wh kg<sup>-1</sup>, and this value was 11 times higher than energy density of KOH electrolyte (5.2 Wh kg<sup>-1</sup>).

The electrochemical properties of SCs, especially their capacitances, are highly dependent on the suitability of the electrode material and the electrolyte. ILs are also heavily influenced by the electrode materials. In carbon material including porous activated carbon (AC), the graphitic edges are twisted, which can lead to uneven charge distribution [36]. This effect is

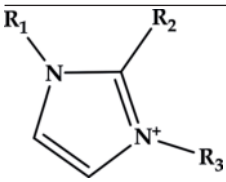
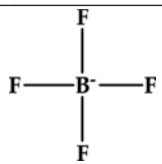
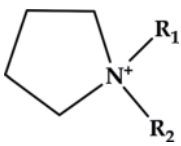
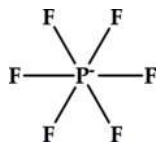
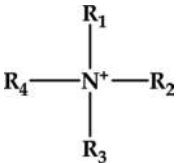
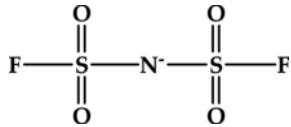
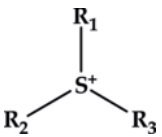
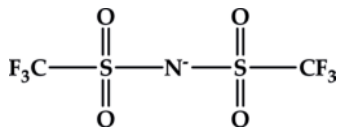
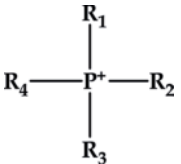
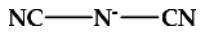
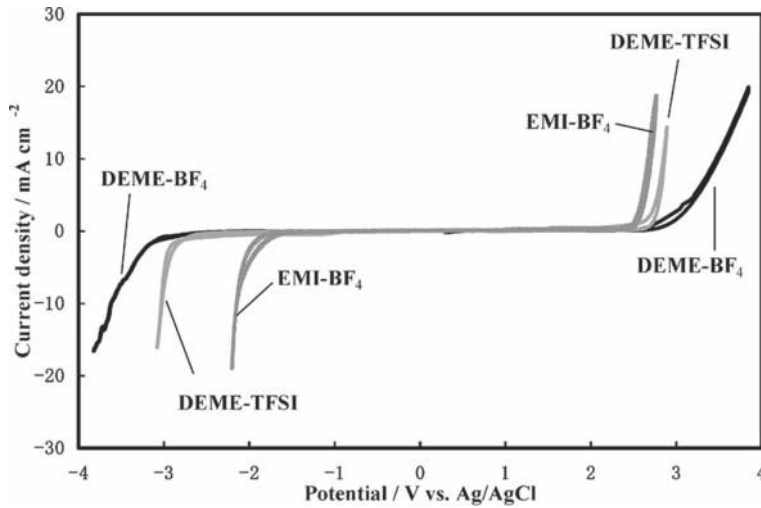
Cation	Anion
 <p>Imidazolium</p>	 <p>Tetrafluoroborate</p>
 <p>Pyrrolidinium</p>	 <p>Hexafluorophosphate</p>
 <p>Ammonium</p>	 <p>Bis(fluorosulfonyl)imide</p>
 <p>Sulfonium</p>	 <p>Bis(trifluoromethylsulfonyl)imide</p>
 <p>Phosphonium</p>	 <p>Dicyanamide</p>

Table 1. Representative cations, anions of ILs for SCs.

more important in ILs because the entire medium is made up of charged ions, so ions interact directly with the localized charge on the electrode surface [37]. Aligned mesoporous carbon provides a good opportunity for diffusion of electroactive species through well-ordered structures, but the chemical composition and degree of graphitization play a decisive role in electrochemical behavior and EDL formation [38]. This effect is more prevalent in ILs, in which the ionic medium is fully interacting. The nature of IL has a profound effect on the capacitive behavior of well-defined mesoporous carbon [39]. Graphene and similar carbonaceous materials are generally covered with various functional groups. Molecular dynamics simulations



**Figure 3.** Cyclic voltammogram of the ionic liquids based on the DEME cation and EMI-BF<sub>4</sub> at 25°C. Scan rate: 1 mV s<sup>-1</sup>, working and counter electrode: Platinum, reference electrode: Ag/AgCl electrode [33]. (DEME: N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium, EMI-BF<sub>4</sub>: [EMI][BF<sub>4</sub>]).

suggest that functional groups, especially hydroxyl groups, prevent ILs ions from interacting directly with the electrode surface [40]. These phenomena can be occurred polarity and hydrophilic/hydrophobic physical property of functional groups. In case of partially negative functional groups of carbonaceous materials like chlorine treated carbon prevent anion adsorption, or hydrophilic ILs indirectly bonded with the functionalities on surface of porous carbon electrode by hydrogen bonding and ions of ILs cannot be penetrated into narrow micropores. These ions block pores, and consequently, the specific capacitance was reduced especially at the high scan rate [41, 42]. Interestingly, these functional groups of carbonaceous materials are helpful to increase the specific capacitance of SCs in conventional electrolytes especially the aqueous electrolytes due to pseudoreaction. Thus, functional groups of carbonaceous materials have disadvantageous for ILs electrolytes system, while they are not effective with the conventional electrolyte adopted SCs. Pinker et al. controlled the specific capacitance by surface treatment of ordered mesoporous carbon [41]. [EMI][BF<sub>4</sub>] was used as the electrolyte. The surface treatment of pristine-ordered mesoporous carbide-derived carbon (OM-CDC) in chlorine gas and oxygen was evaluated. The chlorine gas protects the surface from reoxidation and lowers the surface polarity, thus enhancing the rate capability. The surface treatment of OM-CDC in air introduces oxygen functionalities, which result in a significant decrease of the rate capability. Silicon nanowires coated have attracted attention as a promising candidate for electrolytes for ILs electrolyte-based SCs due to their excellent cycle performance and thermal stability [43, 44]. Since the silicon electrode is not suitable for aqueous electrolytes, the importance of ionic liquid electrolytes has been further emphasized.

Along with the compatibility with the electrodes, the behavior of the ionic liquid at the electrode/electrolyte interface is also important. Without destructive chemical interactions of the IL ion, it is electrochemically stable, but structural changes during cycling are still an important

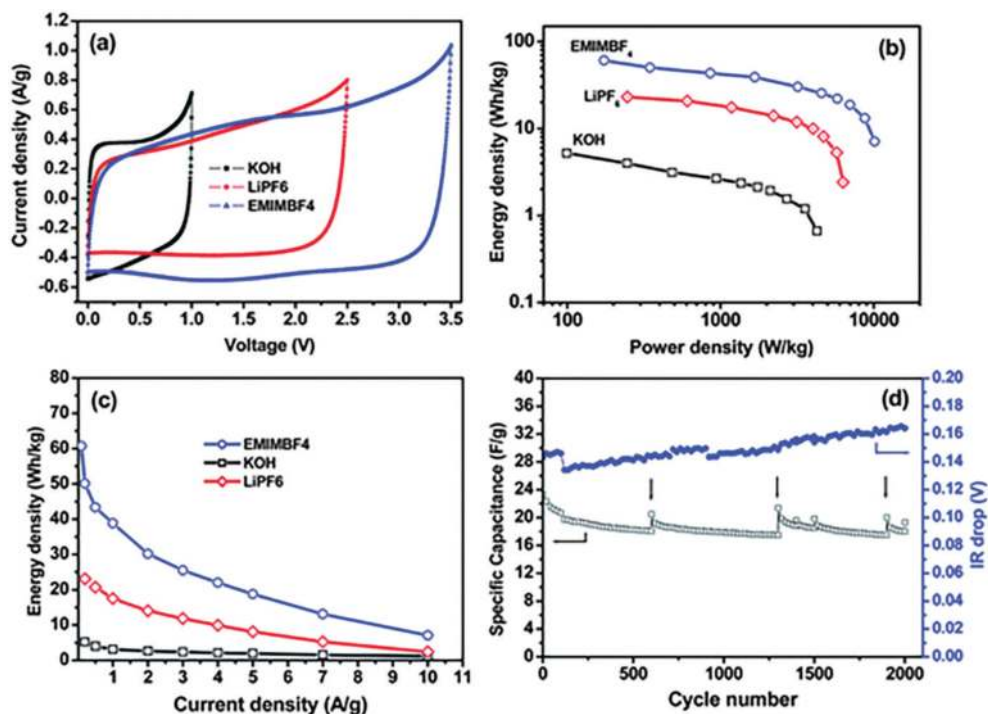


Figure 4. CV behaviors (a), Ragone plots (b), and change of energy density with current density (c) of the RGO-CMK-5 composite electrode measured in different electrolytes. (d) Cycle performance of the RGO-CMK-5 electrode measured in EMIMBF<sub>4</sub> electrolyte, with the arrows showing the beginning of a new cycle [35] (CV: cyclic voltammetry, EMIMBF<sub>4</sub>: [EMIM][BF<sub>4</sub>]).

issue and should be carefully considered. To understand the aging or failure mechanism of ILs, electrochemical decomposition of ILs was investigated using in situ techniques (infrared and electrochemical spectroscopy methods and XPS) [45, 46]. These studies were performed to understand the EDL structure of ILs, enhancing electrochemical properties by modifying positive or negative ions or adopting pseudoelectrode material.

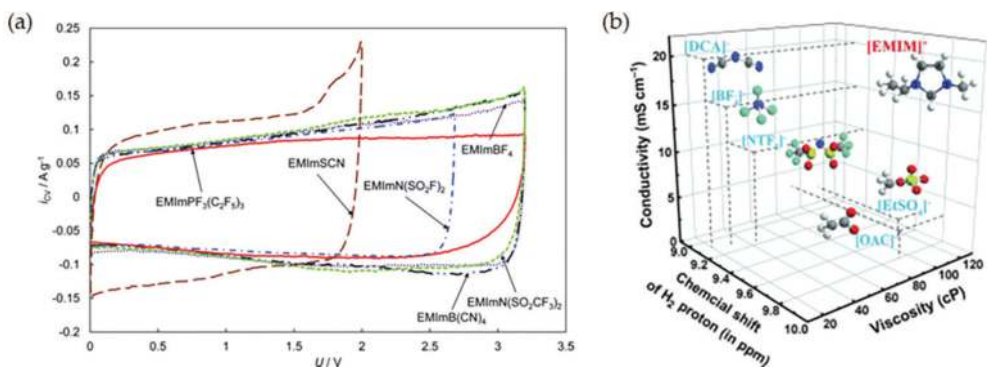
As previously mentioned, imidazolium-based ILs are one of the candidates for SCs electrolyte. The electrochemical characteristics of various ILs electrolytes with [EMI] cations and different anions ([BF<sub>4</sub>], tetracyanoborate([B(CN)<sub>4</sub>]), tris(pentafluoroethyl)trifluorophosphate ([PF<sub>3</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>]), [TFSI], [FSI], and thiocyanate ([SCN])) was reported using carbon cloth electrodes [47]. Working voltage was changed according to anions, and [EMI][BF<sub>4</sub>], [EMI][TFSI], and [EMI][B(CN)<sub>4</sub>] were stable up to 3.2 V. The highest energy values at 3.2 V for [EMI][B(CN)<sub>4</sub>] were 49 Wh kg<sup>-1</sup>. Graphene sheet electrode was also evaluated [EMI] cation with various anions, which were categorized representative chemical species. The five anions were [BF<sub>4</sub>] as inorganic fluoride, [FSI] as organic fluoride, [DCA] as cyano functionality, ethylsulphate ([EtSO<sub>4</sub>]) as ester functionality, and acetate ([OAc]) as acid. The hydrogen-bond-accepting ability of anions was closely related to the viscosity of the ILs. Moreover, [EMI][DCA],



[EMI][BF<sub>4</sub>], and [EMI][FSI] showed excellent cycling stability with the same potential window of 2 V. SCs adopting [EMI][BF<sub>4</sub>] had the widest potential window of 4 V, which displayed a maximum energy density of 67 Wh kg<sup>-1</sup> at a current density of 1 Ag<sup>-1</sup> [48] (**Figure 5**).

Other types of imidazolium-based ILs were also investigated. Bettini et al. studied film SCs by adopting ILs electrolytes. The electrolyte was varied out through cation based on [FSI] anion. The applied cations are EMI, 1-butyl-3-methylimidazolium ([BMI]), 1-dodecyl-3-methylimidazolium ([C<sub>12</sub>MI]), and 1-butyl-1-methylpyrrolidinium ([PYR<sub>14</sub>]), and electrode was nanostructured carbon (ns-C) [49]. The ionic conductivities were decreased depending on cation size in the order of [EMI] > [BMI] > [PYR<sub>14</sub>] > [C<sub>12</sub>MI]. [BMI][FSI] adopted SCs exhibited the highest specific capacitance of 75 F g<sup>-1</sup> despite of secondly high ionic conductivity. This means that [BMI][FSI] have chemical affinity with ns-C. Borges et al. use 1-butyl-2,3-dimethylimidazolium [EBDMI] cation and [TFSI] anion as electrolyte of temperature stable SCs [50]. The proposed electrolyte achieved 4.4 V of electrochemical stability window with functionalized double-walled carbon nanotubes (DWCNT).

The pyrrolidinium cations were extensively studied for the wide operating voltage. Most of cases, [PYR<sub>14</sub>] cation was selected. Largeot et al. introduced high-temperature carbon-carbon SCs working at 100°C with [PYR<sub>14</sub>][TFSI] electrolyte and microporous carbide-derived carbon electrode [51]. High operating temperature means that ILs are thermally stable, and the viscosity of ILs is not enough to obtain reasonable specific capacitance (Most of pyrrolidinium based ILs exist in quasi solid state at room temperature). The specific capacitance of suggested SCs reached a maximum at 130 F g<sup>-1</sup>. Mastragostino group also reported several studies using pyrrolidinium cation, [PYR<sub>14</sub>], [TFIS] was used as anion [52–54]. They tested the ILs electrolytes using hybrid SCs (asymmetric SCs). The AC and the conductive polymer (poly(3-methylthiophene)) were adopted as electrodes. These SCs achieved 3.6 V of the working voltage and 16,000 cycle of the cycle-ability at 60°C. The hybrid supercapacitor delivered 24 Wh kg<sup>-1</sup> and 14 kW kg<sup>-1</sup> as maximum values. However, low ionic conductivity remains as problems.



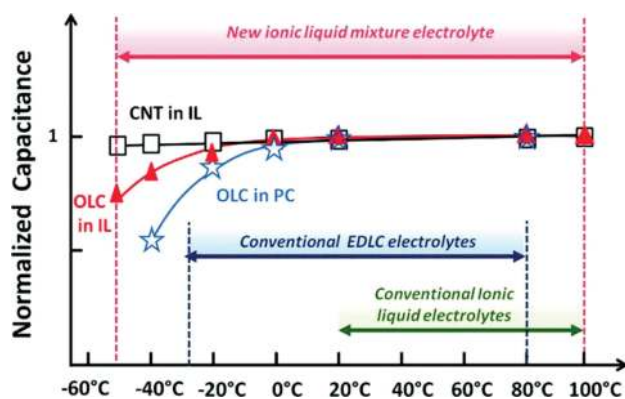
**Figure 5.** (a) Cyclic voltammograms measured at cell voltage scan rate 1 mV s<sup>-1</sup> for SC test cells filled with RTILs. (EMImBF<sub>4</sub>: [EMI][BF<sub>4</sub>], EMImB(CN)<sub>4</sub>: [EMI][B(CN)<sub>4</sub>], EMImPF<sub>6</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>: [EMI][PF<sub>6</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>], EMImN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>: [EMI][TFSI], EMImN(SO<sub>2</sub>F)<sub>2</sub>: [EMI][FSI], and EMImSCN: [EMI][SCN]) [47], (b) the relationship between the electrical conductivity, viscosity, and <sup>1</sup>H NMR chemical shift of the proton in the 2-position of the imidazole ring of the ILs studied [48].

To overcome the viscosity issue, factionalized electrodes were proposed. Nitrogen-doped reduced graphene oxide aerogel (N-rGO aerogel) was one of them [55].  $[\text{PYR}_{14}][\text{DCA}]$  was matched with N-rGO aerogel. Reported SCs show excellent electrochemical characteristics of wide working potential of 4.0 V, high specific capacitance of  $764.53 \text{ F g}^{-1}$  at  $1 \text{ A g}^{-1}$ , and a capacity retention of 86% over 3000 charge discharge cycles, and this system provided maximum specific power of  $6525.56 \text{ W kg}^{-1}$  and energy of  $245.00 \text{ Wh kg}^{-1}$ . In addition, ILs with various cations have been studied as electrolytes. The sulfonium and the piperidinium were also investigated to achieve high electrochemical performances [31, 56]. However, these ILs have relatively high melting point about  $40\text{--}60^\circ\text{C}$ ; thus, they applied as electrolytes for high-temperature SCs or as electrolytes with solvents.

## 2.2. Other approaches of ionic liquid as liquid electrolyte

Approach for reducing the viscosity of ILs is anion eutectic ILs mixture. Several studies were reported to reduce melting transitions and an enhance liquids range, pyrrolidinium- and piperidinium-based ILs which have relatively high viscosity as previously mentioned were selected [57–59]. SC with mixed ILs gave the assurance that the eutectic mixture of ILs could dramatically extend the temperature range of the electrical energy storage device. This is a sufficient result to dispel the recognition that the ILs cannot be used as a low-temperature electrolyte due to the high viscosity of them. SC with mixed ILs showed electrical double layer capacitors able to operate from  $-50$  to  $100^\circ\text{C}$  over a wide voltage window (up to 3.7 V) and at very high charge discharge rates of up to  $20 \text{ V s}^{-1}$  [59]. **Figure 6** shows the change of specific capacitance versus the temperature according to various electrolytes.

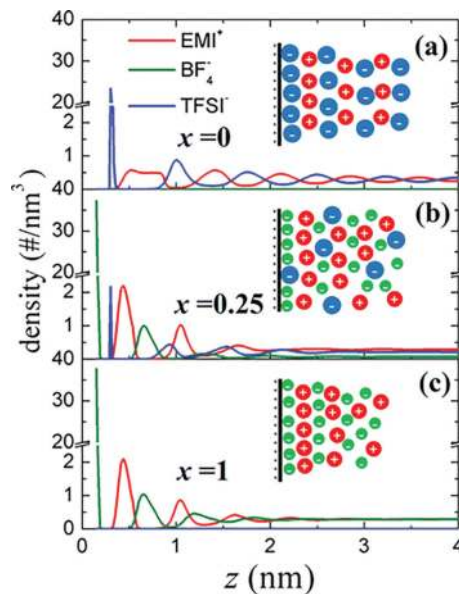
Recently, Lian et al. introduced mixed anion ILs in order to have the same cations but having two types of anions with different sizes and geometries for enhancing the capacitive



**Figure 6.** Normalized capacitance ( $C/C_{20^\circ\text{C}}$ ) for the onion like carbon and vertical aligned-CNT electrodes (new ionic liquid mixture electrolyte:  $([\text{PIP}_{13}][\text{FSI}])_{0.5}([\text{PYR}_{14}][\text{FSI}])_{0.5}$ , conventional EDLC electrolyte: 1 M of  $[\text{Et}_4\text{N}][\text{BF}_4]$  in PC, and  $[\text{PIP}_{13}]$ : N-methyl-N-propylpiperidinium). Capacitances were calculated at  $100 \text{ mV s}^{-1}$ , except for the  $-50^\circ\text{C}$  ( $1 \text{ mV s}^{-1}$ ) and  $-40^\circ\text{C}$  ( $5 \text{ mV s}^{-1}$ ) experiments. This plot shows that the use of the IL mixture extends the temperature range for supercapacitors into the  $-50$  to  $100^\circ\text{C}$  range, while conventional electrolytes using PC as solvent are limited to the  $-30$  to  $80^\circ\text{C}$  range.  $C_{20^\circ\text{C}}$  was 80 and 4 mF, respectively, for OLC and VA-CNT cells. All cells were cycled from 0 up to 2.8 V [59].

performance [60]. This research provided the capacitive behavior of a planar carbon in two kinds of ILs and their mixture both experimentally and computationally. They selected single cation [EMI] and two different anions of  $[BF_4]$  and [TFSI]. This study explained that the mixture effect, which makes more counterions pack on and more co-ions leave from the electrode surface, leads to an increase of the counterion density within the EDL and thus a larger capacitance. **Figure 7** compares the distribution of ions at the electrode surface in pure ILs electrolyte and their mixture.

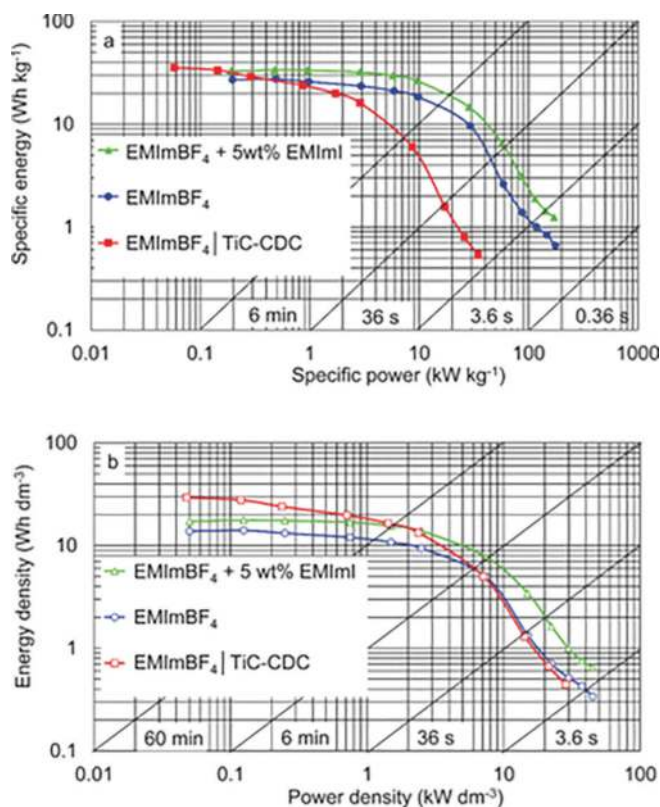
Another approach for ILs is redox active electrolyte. Until recently, SCs using redox reactions have been studied with electrodes. As a result, various electrode materials such as metal oxides and conductive polymers have been proposed [61–63]. These pseudomaterials have been mostly studied using aqueous electrolytes because of the redox mechanism using proton. However, application of ILs has been studied as alternatives due to the limitation of the operating voltage of aqueous electrolyte and the inadequacy of surface functionality of electrode materials. Protic ILs which contain proton were investigated as the electrolyte for pseudo-type electrode. Protic ILs are advantageous over aprotic ILs; however, the high viscosity and slow proton transfer in the ILs electrolyte could limit the charging rate [64, 65]. And their cycle-ability was not enough to actual application. Aprotic ILs were tried as electrolyte for pseudoelectrode in some cases [66]. The pseudomaterial was manganese dioxide ( $MnO_2$ ), and the IL was [BMI][DCA]. The redox mechanisms between ILs and  $MnO_2$  were expressed in Eq. (3). Within a potential range of 3 V, a specific capacitance of 70 F g<sup>-1</sup> was obtained.



**Figure 7.** (a) Schematic representation of a ILs mixture near the electrode surface, (b) distributions of cations (red line for [EMI]) and anions (green line for  $[BF_4]$  and blue line for [TFSI]) in EDL of pure and mixed ILs near a positive surface with positively charged surface = 1.5 V: (a)  $x = 0$ , (b)  $x = 0.25$ , and (c)  $x = 1$ . The inserts are schematics of the EDL structures. ( $x$  is the weight fraction of [EMI][TFSI]) [61].



A new strategy has been explored to increase the capacitance of SCs by inducing the pseudocapacitive contribution from the redox-active electrolytes [67]. The Faradaic reactions occur in the electrolyte, which can contribute extra capacitance to the SCs. In this case, the pseudocapacitance is not only contributed by the pseudocapacitive electrode materials but can also be contributed from the electrolyte. The introduced redox mediator was halide (mostly iodide), vanadium (IV) oxide sulfate ( $VOSO_4$ ), metal cation ( $Cu^{2+}$ ), heteropoly acids, fractionalized arene, and quinode-benzoide [67–71]. As mentioned previously, most of redox couple were applied with aqueous medium. However, to achieve higher cell voltage and thus a higher energy density, a number of nonaqueous electrolytes including organic and IL-based electrolytes have been studied and reported. In the case of ILs, halide ion species was used as



**Figure 8.** (a) Specific energy vs. specific power and (b) energy density vs. power density plots for EDLCs based on microporous-mesoporous carbon electrodes in EMImBF<sub>4</sub> + 5 wt% EMImI mixture (triangles), in neat EMImBF<sub>4</sub> (circles), obtained from constant power tests within the cell potential range from 2.4 to 0.4 V and for comparison for EDLCs based on TiC-CDC carbon electrodes in EMImBF<sub>4</sub> (squares), and obtained from constant power tests within the cell potential range from 3.0 to 1.5 V. (EMImBF<sub>4</sub>: [EMI][BF<sub>4</sub>] and EMImI: [EMI][I]) [74].

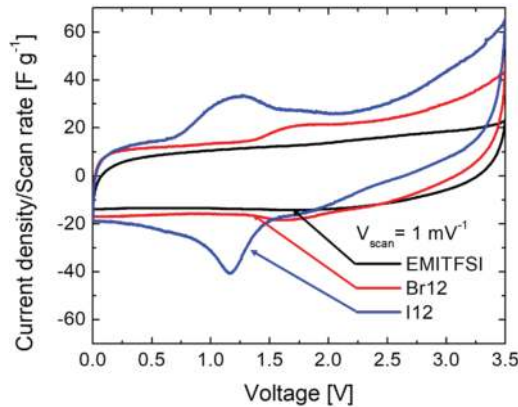


Figure 9. Cyclo-voltammogram of [EMI][TFSI] and [EMI][I and Br]/[EMI][TFSI] mixture at  $1 \text{ mV s}^{-1}$ .

redox active couple. Taniki et al. reported that the N-ethyl-N-methylpyrrolidinium ([EMPyr]) fluoro-hydrogenate ( $[(\text{FH})_{2,3}\text{F}]$ ) could significantly contribute extra specific capacitance to the SCs through the redox reaction of the electrolyte [72]. In the case of charging up to 2.5 V, the EDL capacitance of the positive electrode is  $140 \text{ F g}^{-1}$ , and the redox capacitance is  $150 \text{ F g}^{-1}$ , both of which contribute to the total capacitance. Correspondingly, the negative capacitance is the sum of the double-layer capacitance of  $130 \text{ F g}^{-1}$  and the redox capacitance of  $116 \text{ F g}^{-1}$ . In 2014, Tooming et al. reported redox active electrolyte using 5 wt% [EMI] iodide into [EMI][BF<sub>4</sub>], and they archive a nearly 50% increase in specific capacitance in comparison to bare [EMI][BF<sub>4</sub>] [73]. As shown in Figure 8, noticeable increase in specific power and power density ( $\sim 30\%$  at  $P \sim 1 \text{ kW kg}^{-1} / 1 \text{ kW dm}^{-3}$ ) as well as in specific energy and energy density ( $\sim 60\%$  at  $P \sim 1 \text{ Wh kg}^{-1} / 1 \text{ Wh dm}^{-3}$ ) has been achieved by 5 wt% addition of [EMI][I] into [EMI][BF<sub>4</sub>].

However, EDL capacitance is proportional to number of the ions (charges). Thus, weight ratio is not appropriate for comparing [EMI][I]/[EMI][BF<sub>4</sub>] mixture and neat [EMI][BF<sub>4</sub>]. For this reason, our group suggested redox active electrolyte, which have same number of ions. We choose bromide and iodide as redox mediator. The specific capacitances were increased by amount of [EMI] halide (Figure 9). The SCs adopting 0.12 mole fraction of [EMI][I] show the highest specific capacity of  $176.1 \text{ F g}^{-1}$  with 3.5 V of working voltage. The energy density is  $231.9 \text{ Wh kg}^{-1}$  at  $0.5 \text{ A g}^{-1}$ , when the power density is  $2705.6 \text{ W kg}^{-1}$ .

### 3. Ionic liquid as quasi solid and solid electrolyte

Liquid electrolytes need additional encapsulation. Thus, SCs applied ILs face difficulty in integration and manufacturing flexible devices. These problems can be addressed by solidifying the ILs because the ILs maintain the conductivity even when solidified, unlike a typical organic electrolyte. Generally, polymers are applied for solid state with various devices, and ILs adopted polymer structure are described in Figure 10.

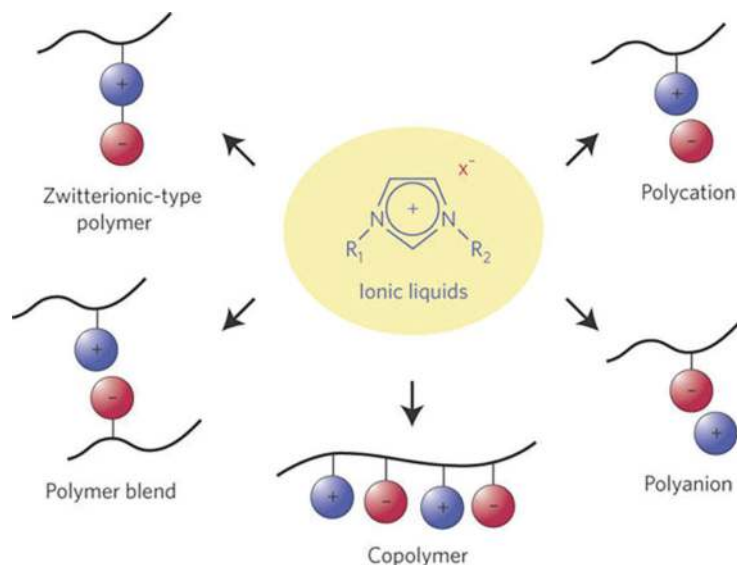
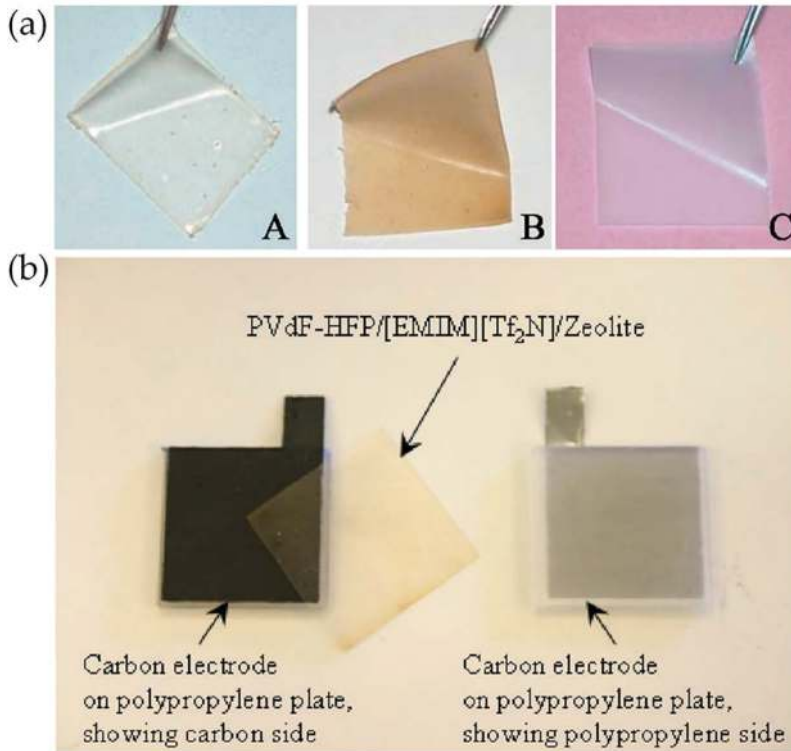


Figure 10. Ionic liquid-polymer electrolyte.

### 3.1. Ionic liquid-blended polymer electrolyte

ILs blended polymer electrolyte can be referred to ion gel (iongel, ionogel) because most of the ILs blended polymer electrolytes were synthesized in gel polymer type. The initial gel polymer electrolyte consisted of ion conducting salts (ILs), organic solvent, and polymers like gel polymer electrolyte of LIBs. In 1997, Fuller et al. reported iongel that contains ILs, organic solvent, and poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) [74]. The iongel which was composed of [EMI][BF<sub>4</sub>] and [EMI][CF<sub>3</sub>SO<sub>3</sub>]<sup>-</sup> and PVdF-HFP achieved the highest ionic conductivity of 5.8 mS cm<sup>-1</sup>. Various carbon materials were adopted from classical AC to nanostructured carbon such as CNT and graphene [75–77]. Pandey et al. also proposed [EMI][B(CN)<sub>4</sub>] and PVdF-HFP-based iongel electrolyte [77]. SCs applied ion gel was tested with multiwall carbon nanotube (MWCNT) electrode. The SCs adopting [EMI][B(CN)<sub>4</sub>] based iongel shows good thermal stability up to 310°C, a wider electrochemical window of ~3.8 V, and a high ionic conductivity of  $\sim 9 \times 10^{-3}$  S cm<sup>-1</sup> at room temperature. The SCs also show a specific energy of ~3.5 W h kg<sup>-1</sup> and a specific power of ~4.2 kW kg<sup>-1</sup>. Lu et al. also studied ion gel with PVdF-HFP and [EMI][FSI] [78]. They compared different polymer composites. The ion gels were flexible and mechanically strong and show 28 Wh kg<sup>-1</sup> of the energy density with 2317 W kg<sup>-1</sup> of the power density. The features of iongel and the structure of the SCs using the iongel are shown in **Figure 11**.

Each carbon electrode was attached on a polypropylene plate on the aluminum foil side. ([EMIM][Tf<sub>2</sub>N]: [EMI][FSI] and PTFE: Poly(tetrafluoroethylene)) [78]. Other type of polymers and ILs has been tried as ion gel electrolyte. Tamilarasan et al. reported ion gel as stretchable electrolyte. The synthesized [BMI][TFSI] incorporated stretchable poly(methyl methacrylate)(PMMA) electrolyte [79]. The device has specific capacitance of 83 F g<sup>-1</sup>,



**Figure 11.** (a) Photographs of ILGPEs prepared by different methods: (A) PVdF-HFP/EMIM][Tf<sub>2</sub>N] by ionic-liquid-polymer gelation method, (B) PVdF-HFP/[EMIM][Tf<sub>2</sub>N]/zeolite by ionic-liquid-inorganic-polymer composite method, and (C) PTFE/[EMIM][Tf<sub>2</sub>N] by ionic-liquid-polymer membrane method. (b) Photograph of a capacitor before assembly from two carbon electrodes and a PVdF-HFP/[EMIM][Tf<sub>2</sub>N]/zeolite ILGPE.

specific current of 2.67 A g<sup>-1</sup>, and energy density and power density of 25.7 Wh kg<sup>-1</sup> and 35.2 kW kg<sup>-1</sup>, respectively. The ion gel stretched up to 150%. Other polymeric matrixes such as poly(acrylonitrile), polyvinylidene fluoride/polyvinyl acetate, poly(ethylene oxide), poly(vinylalcohol), poly(methylmethacrylate), poly(tetrafluoroethylene), and chitosan were investigated [80–83].

Most of the introduced ILs and iongel operated at 2.0–3.5 V. These operating voltages were not enough to overcome intrinsic limitation of ILs because ILs have low ionic conductivity and high viscosity, such properties cause decrement of specific capacity. To overcome relatively low specific capacity, operating voltage have to be enhanced at 3.5–4.0 V. Additionally, high operating voltage is helpful to manage power supply. SCs are regarded as excellent energy storage devices due to their high power density and permanent life cycles. However, SCs face with critical challenge of low energy density. Therefore, LIBs and SCs are applied together for the complementary purpose. The typical case is a wireless detection system that needs two kinds of power supply units. One is a continuous power supply for operation, and the other is a pulse power to transmit data to the control system. Continuous power systems require

high-energy densities, while pulse power systems need high-power densities. Consequently, LIBs are responsible for device operation, while SCs are used for data transmission. A critical issue in this system is voltage leveling between the LIBs and SCs. The operating voltage of LIBs is from 3.5 to 4.0 V. Thus two or more SCs in series are needed for a wireless detection system. If SCs achieve the 3.5–4.0 V rated voltage with high energy densities or LIBs achieve high power densities, then the power supply unit can be minimized and integrated. LIBs have intrinsic limitations in power densities due to their energy storage mechanisms. Hence, SCs that show high energy densities and wide operating voltages have been researched extensively. Thus, new approaches were reported to enhance working voltage of SCs. Pandey et al. adopted zeolite as additives for enhancing operating voltage, and the zeolite added SCs was stable up to 4.1 V [78]. Cross-linked polymer matrix was suggested as solid electrolyte for high-voltage SCs. Choi et al. suggested all printable SCs using UV curable materials. [BMI][BF<sub>4</sub>] and UV-cured ethoxylated trimethylolpropane triacrylate (ETPTA)-based gel polymer electrolytes are incorporated to produce the solid-state SCs. They showed various shapes of inkjet-printed SCs described in **Figure 12**. Interestingly, proposed UV-cured ion gel was water proof despite of adopting [BMI][BF<sub>4</sub>] [84].

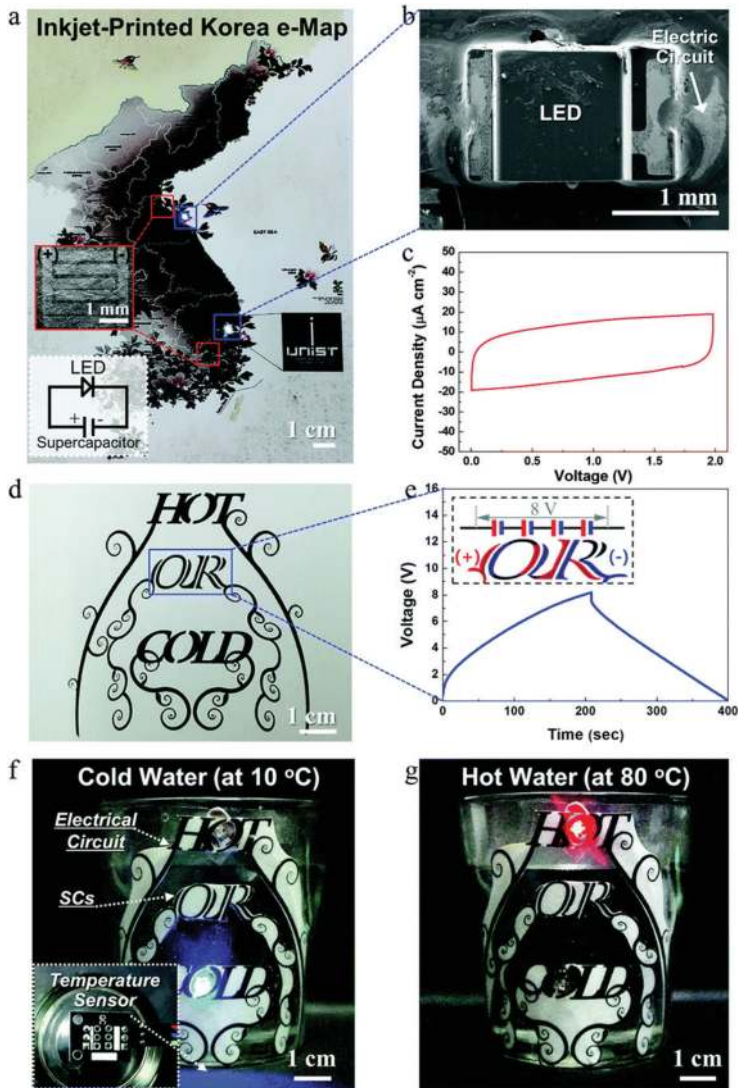
Our team proposed a quasi-solid polymer electrolyte based on a composite cross-linked poly-4-vinylphenol (c-P<sub>4</sub>VPh) embedded [EMI][TFSI] [5]. [EMI][TFSI] was selected for its high ionic conductivity, and c-P<sub>4</sub>VPh was used for its ability to enhance electrochemical stability by hydrogen bonding between [EMI][TFSI] and c-P<sub>4</sub>VPh in addition to maintaining a quasi-solid state. Also, cross-linked polymers can keep a larger amount of ILs than other polymer by swelling. The composite electrolytes are highly ionic conductive solid state due to the rigid framework of c-P<sub>4</sub>VPh and high ionic conductivity from large contents of [EMI][TFSI] over 60 wt%. The IL-CPs are thermally stable over 300°C and electrochemically stable over 7.0 V, since there are hydrogen bonds between c-P<sub>4</sub>VPh and [EMI][TFSI]. We also introduced all-solid state SCs that operate at 4.0 V and have high energy density without sacrificing power density. SCs showed the best electrochemical performances and had capacitance of 172.5 F g<sup>-1</sup> and energy density of 72.3 Wh kg<sup>-1</sup>. Their structure and electrochemical characteristics are displayed in **Figure 13**.

### 3.2. Poly ionic liquid as solid electrolyte

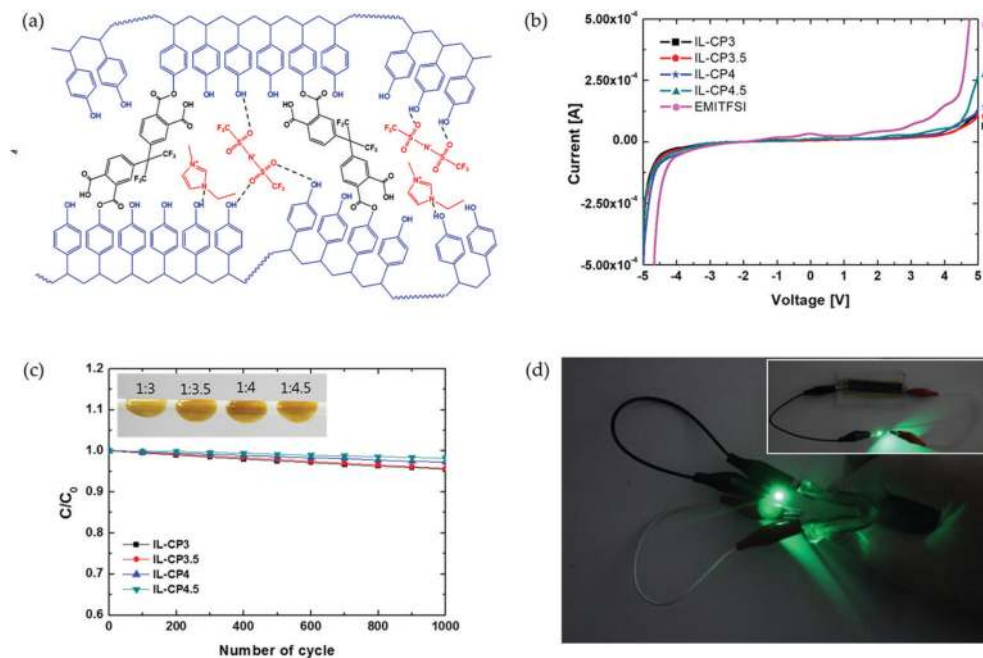
A poly IL (PIL) or polymeric ionic liquid is a polymer electrolyte containing a polymer backbone and an IL species in the monomer repeat unit. Certain characteristics of IL such as negligible vapor pressure, thermal stability, nonflammability, relatively high ionic conductivity, and broad electrochemical stability window are transferred to the polymer chain (from oligomers to high molecular weight polymers) [85]. Various PIL structures and properties are required for various applications of polymer electrolytes, electrochemical devices, smart materials, catalyst supports, porous polymer structures, and antibacterial PILs. The standard synthetic pathway for PILs relies on a basic strategy: (1) direct chain growth polymerization of IL with or without nonionic monomers; (2) step-growth polymerization of IL monomers; and (3) post-modification of polymer chains with IL monomers.

Properties required as solid electrolytes include ionic conductivity, thermal stability, and electrochemical stability. The ionic conductivity of PILs is an important property when applied as





**Figure 12.** Esthetic versatility and IoT applications of the inkjet-printed SCs as object-tailored/monolithically integrated power sources. (a) Photograph of the inkjet-printed Korea map, wherein the inkjet-printed SCs (marked by red boxes) were seamlessly connected to LED lamps (marked by blue boxes) via the inkjet-printed electric circuits. (b) SEM image of the LED lamp connected to the inkjet-printed electric circuits. (c) CV profile (scan rate = 1.0 mV s<sup>-1</sup>) of the inkjet-printed SC in the map. (d) Photograph of the inkjet-printed, letter (“OR”)-shaped SCs that were seamlessly connected to the letter (“HOT” and “COLD”)-shaped electric circuits onto A4 paper. (e) Galvanostatic charge/discharge profile (current density = 1.0 mA cm<sup>-2</sup>) of the inkjet-printed, letter (“OR”)-shaped SCs that were composed of 4 cells connected in series. (f) Photograph depicting the operation of the blue LED lamp in the smart cup (for cold water (~10°C)), wherein the inset is a photograph of a temperature sensor assembled with an Arduino board. (g) Photograph depicting the operation of the red LED lamp in the smart cup (for hot water (~80°C)) [84].



**Figure 13.** (a) Chemical structure of IL-CPs, (b) LSV for EMITFSI and IL-CPs in the SUS/SUS cell (CR 2032), (c) flexibility of IL-CPs and bending performance of SCs with IL-CPs for 1000 cycles, and (d) photograph of a green light-emitting diode (LED) powered by a single SC with IL-CP3.5. (IL-CPs: [EMI][TFSI]/c-P<sub>4</sub>VPh composite, and IL-CPx: x = weight ratio of [EMI][TFSI]) [5].

a solid electrolyte. Unlike ILs and ion gels in which both anions and cations can move, PILs are typically single-ion conductors. In this case, anions or cations are structurally constrained as part of the polymer skeleton [86]. Therefore, the ionic conductivity of PIL is generally lower than that of monomeric ILs ionic conductivity. This phenomenon is due to the significant increment of glass transition temperature ( $T_g$ ) and depletion of mobile ions after covalent or ionic bonding [85]. The ionic conductivity of PIL is affected by polymer architecture, molecular weight, and chemical nature of polymer chains.

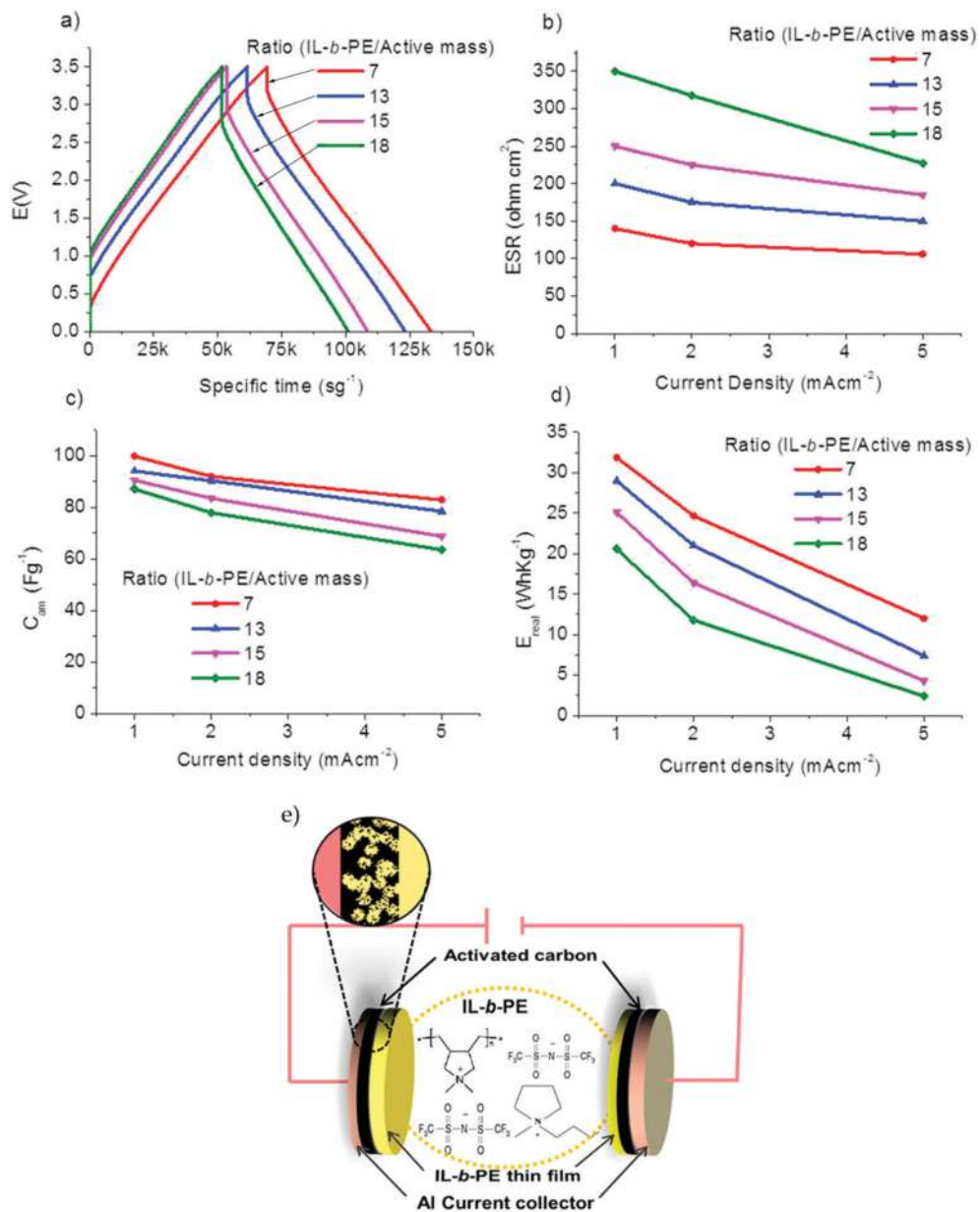
Particularly, the ionic conductivity of PIL is related to the glass transition temperature, and the ionic conductivity is usually increased when the  $T_g$  is low. PIL has weak binding ions and can exhibit low  $T_g$  despite having very high charge densities due to weak electrostatic ion pair interactions. Counter ions affect the  $T_g$  of these polymers. Therefore, a method of lowering the  $T_g$  using a different kind of anion has been proposed. Tang et al. found that anion tendency with poly 1-(p-Vinylbenzyl)-3-methyl-imidazolium cation, the  $T_g$  also changes in order [FSI] (3°C) < o-benzoic sulphimide (40°C) < [BF<sub>4</sub>] (78°C) < [PF<sub>6</sub>] (85°C) [87]. For PILs with the same anion [BF<sub>4</sub>], the  $T_g$  varied according to the backbone and Poly[(1-butylimidazolium-3)methyl-ethylene oxide (33°C) < 1-[2-(Methacryloyloxy)ethyl]-3-butyl-imidazolium (54°C) < Poly[1-(p-Vinylbenzyl)-3-butyl-imidazolium (78°C) < poly 1-(p-Vinylbenzyl)-3-methyl-imidazolium

(110°C). Flexible backbones yield lower  $T_g$  values. Similarly, Hu et al. directly grafted TFSI anions onto the polyethylene oxide backbone via anionic ring-opening polymerization [88]. The resulting PIL exhibits a low  $T_g$  value (up to -14°C) and an average conductivity of  $10^{-5}$  S cm<sup>-1</sup> at 30°C and  $\sim 10^{-3}$  S cm<sup>-1</sup> at 90°C.

The thermal stability of the PILs is directly related to the lifetime and stability of the capacitor and chemical and electrochemical stability. In thermogravimetric analysis (TGA) experiments, the decomposition starting temperature ( $T_{\text{onset}}$ ) is usually controlled through the nature of the PIL backbone chemical structure. Imidazolium-based PILs have improved thermal stability due to conjugate structure and steric hindrance. They have higher  $T_{\text{onset}}$  values than pyrrolidinium-based PILs. The thermal stability of PILs increases with the length of the substituent of the cation. The chemical structure of anions also affects the  $T_{\text{onset}}$  value of PILs. Poly (1-vinyl-3-ethyl-imazazolium) X-PIL was studied by comparing the effects of counter anions on PIL thermal stability [89].  $[\text{CF}_3\text{SO}_3^-] > [\text{TFSI}] > [\text{C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{SO}_3^-] > [\text{PF}_6] > \text{bromide} > [\text{C}_{16}\text{H}_{34}\text{PO}_4^-]$ .

PIL-based polymer electrolytes have high ionic conductivity (up to  $10^{-3}$  S cm<sup>-1</sup> at 25°C), wide electrochemical windows (up to 5 V), and high thermal stability (up to 350°C) [86]. Pyrrolidinium-based PILs have been reported to have better electrochemical stability than imidazolium-based PILs. The pyrrolidinium cations also exhibit a much larger cathodic electrolysis potential than the quaternary ammonium cations of the noncyclic and unsaturated rings [90]. Because of excellent electrochemical stability and reasonable ionic conductivity in solid phase, PIL electrolytes have been considered as an ideal electrolyte for supercapacitors. However, only a few studies have been reported in this area by Marcilla group, and (Diallyldimethylammonium) bis (trifluoromethanesulfonyl) imide dissolved in [PYR<sub>14</sub>] was prepared and applied as a solid state electrolyte [91, 92]. Impregnating the electrode with the electrolyte before assembling the SCs is an important process for improving the carbon-electrolyte contact. However, these manufactured SCs high ESR values due to poor electrode/electrolyte interface performance. Further studies using pyrrolidinium-based PIL electrolytes with high ionic conductivity have greatly improved relative dielectric constant. **Figure 14** shows the PILs structure and electrochemical characteristics.

In conclusion, ILs have tremendous potential in electrochemical systems with combination of cations and anion. However, their applicability has been limited by the general perception that they are ionic electrolytes for replacing conventional electrolytes. However, due to its high viscosity, low ionic conductivity, and high price, it is difficult to replace conventional electrolytes directly. In other words, ILs should not be chosen as an alternative to organic solvents. Therefore, it is considered that the ILs-based liquid electrolyte are used to enhance the energy density by increasing the high operating voltage of the SCs. They are also helpful to secure the stability and safety of SCs. In addition, since IL is stable at high temperatures, it can be applied to SCs that must be used under extreme conditions. In the same way, IL is more attractive as a solid electrolyte instead of a conventional electrolyte. In particular, IL-based solid polymer electrolytes appear to be one of the most promising choices for flexible SCs. However, current research on ILs as electrolytes has focused on several ILs, including imidazolium and pyrrolidinium cation. As mentioned, ILs have design flexibility due to the



**Figure 14.** Charge–discharge characterization of all-solid state supercapacitors with different impregnation ratios. (a) Charge–discharge profiles from 0 to 3.5 V at 1 mAcm<sup>-2</sup>, (b) equivalent series resistance (ESR), (c) specific capacitance (C<sub>am</sub>), (d) specific real energy (E<sub>real</sub>) from charge–discharge profiles at different current densities and (e) schematic representation of all-solid state supercapacitors. (IL-b-PE: Ionic liquid based polymer electrolyte).

numerous possible combinations of anions and cations. We believe this flexibility should be achieved by designing a new type of supercapacitor by thinking outside the box beyond what is available.

## Author details

Jeeyoung Yoo

Address all correspondence to: [jyoo78@snu.ac.kr](mailto:jyoo78@snu.ac.kr)

Program in Nano Science and Technology, Graduate School of Convergence Science and Technology, Seoul National University, Seoul, Republic of Korea

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