



# Prospects and Design Insights of Neat Ionic Liquids as Supercapacitor Electrolytes

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Ionic liquids present an opportunity to design efficient electrolytes for supercapacitors, which are among the most extensively studied electrochemical energy storage systems. Ionic liquids are promising candidates for supercapacitor electrolytes because they can eliminate issues associated with aqueous and organic solvent-based electrolytes, such as narrow operating potential windows, safety, and performance. The full potential of ionic liquids as electrolytes in supercapacitors need to be further explored due to promising previous efforts invested in ionic liquid-based electrolyte systems for supercapacitor. This review aims to provide an outlook on neat (pure) ionic liquids applied as supercapacitor electrolytes to isolate the prospects and influences of ionic liquids in supercapacitor electrolyte systems. This work primarily focuses on ionic liquid chemistry links to their performance in supercapacitor electrolytes. Deduced features of importance to supercapacitor performance include the presence of functional groups in the ionic liquids, the ionic liquids physicochemical and electrochemical properties. With the different classes of ionic liquids evaluated, ion size-pore size matching of ionic liquid electrolytes and electrode materials, respectively, affect resulting capacitances and energy densities. Several design strategies to enhance supercapacitor performance by improving ionic liquid transport and electrochemical properties are proposed. The proposed strategies and obtained insights consequently informed further discussions on challenges associated with the commercialization of ionic liquids electrolytes.

**Keywords:** ionic liquids, supercapacitor, electrolyte, design strategies, mechanism, pseudocapacitor, hybrid capacitor, challenges

## INTRODUCTION

Supercapacitors (SC) are electrochemical energy storage systems that play a significant role in addressing the global challenge of integrating renewable energy sources into the energy mix. Electrolytes are major components of electrochemical energy storage systems like SC. The functions of electrolytes include; transporting reactants or supporting species in bulk and providing electronic insulation between the electrodes/terminals (Dühnen et al., 2020). Currently applied electrolytes in electrochemical energy storage devices include aqueous (Susantyoko et al., 2019; Huang et al., 2019; Sharma et al., 2020; Sundaram and Appadoo, 2020; Minakshi Sundaram et al., 2016), organic solvents (Xia et al., 2017), deep eutectic solvents (Dinh et al., 2020; Jaumaux et al., 2020), and ionic liquids (ILs) (Gunday et al., 2019; Gunday et al., 2020; Martins and Torresi, 2018; Chellappan et al., 2020). In SC, organic solvent-based electrolytes particularly suffer from various drawbacks like; high cost, safety issues, cumbersome synthesis and purification procedures

and, low ionic conductivity (Bamgbopa et al., 2017). Hence, there is a need to develop electrolyte systems, which are free from these drawbacks.

SC can be divided into three classes according to the charge storage mechanism: 1) electric double-layer capacitors (EDLC), 2) pseudocapacitor and 3) hybrid supercapacitors (Pal et al., 2019). The EDLC stores charge by the formation of an electric double layer on the electrode-electrolyte interface. The electric double layer formation is due to the adsorption of ions (cations and anions) on the respective electrodes. The fast diffusion of the ions in the electrolyte contributes to the high-power density of EDLC. In pseudocapacitor, the energy is stored by the reversible redox reactions with rapid intercalation of electrolyte ions on the electrodes surface and the electric double layer formation. Hybrid SC is a combination of EDLC and pseudocapacitor, and it displayed superior performance because it combines the charge storage mechanism of both EDLC and pseudocapacitor (Muzaffar et al., 2019). A more detailed description of the supercapacitor types and their charge storage mechanism can be found elsewhere (Raza et al., 2018) (Pal et al., 2019).

Rapid storage and release of energy are peculiar characteristics of SC because of their faster charge-discharge process, which is limited by diffusion. Equivalent specific capacitance ( $C_{eq}$ , in  $\text{Fg}^{-1}$ ), is the primary criteria used to evaluate the performance of a SC electrode material. The specific capacitance of a SC can be calculated from charge-discharge curves using Eq. 1, with energy density defined by Eq. 2.

$$C_{eq} = \frac{\Delta t \int I dt}{m \int V dt} \quad (1)$$

$$\text{Energy Density} = \frac{\int I V dt}{m} \quad (2)$$

where  $I$  is the current during the discharging process,  $m$  is the mass of the active electrode material,  $V$  is the recorded potential of the device and  $\Delta t$  is the total discharge time. As can be seen from Eq 2, a significant increase in the energy density can be achieved by widening the operating potential window of the SC. ILs receive much attention as SC electrolytes primarily due to the possibility of wider electrochemical potential windows (Lei et al., 2013; DeVos et al., 2014), which can significantly help SCs achieve higher energy densities compared to applying aqueous electrolytes. In addition, most neat IL electrolytes can be operated at elevated temperatures ( $>100^\circ\text{C}$ ) because of their high thermal stability and non-flammable nature (Torrecilla et al., 2008) compared to organic solvents. ILs are also associated with remarkable properties such as; being liquids state in a wide temperature range, negligible vapour pressure, high thermal stability (Wasserscheid and Welton, 2008; Van Aken et al., 2015; Lethesh et al., 2014b). The higher electrochemical stability and thermal stability of ILs make them suitable for developing high voltage and high-temperature SC (Zhang et al., 2018).

ILs are organic salts made up of cations and anions with a melting point preferably below  $100^\circ\text{C}$  (Hallett and Welton, 2011; Abbas et al., 2015; Lethesh et al., 2012). If they remain liquids at ambient conditions, they are termed room temperature ionic liquids (Tokuda et al., 2006; Welton, 2018; Venkatraman et al., 2019). The most used anions and cations for the synthesis of ILs are given in Figure 1. ILs are mainly classified into four groups:

aprotic (Esperança et al., 2010), protic (Greaves and Drummond, 2008), zwitterionic (Wu et al., 2018; Grössereid et al., 2019), and functionalized (task-specific) (Davis, 2004; Butt et al., 2020) ILs (Figure 1).

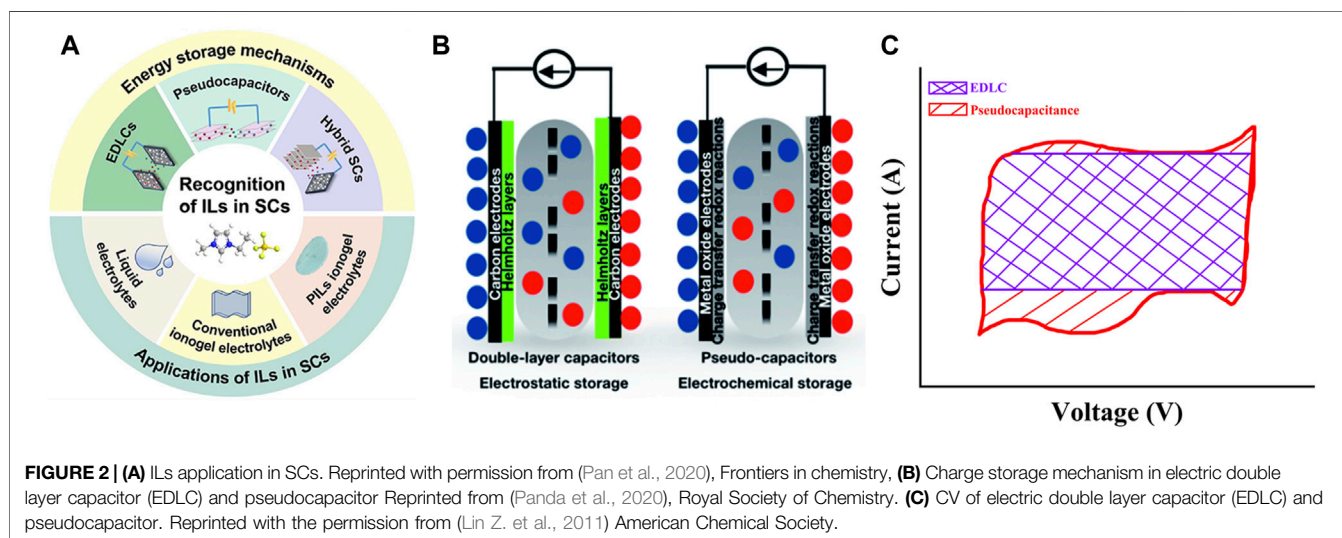
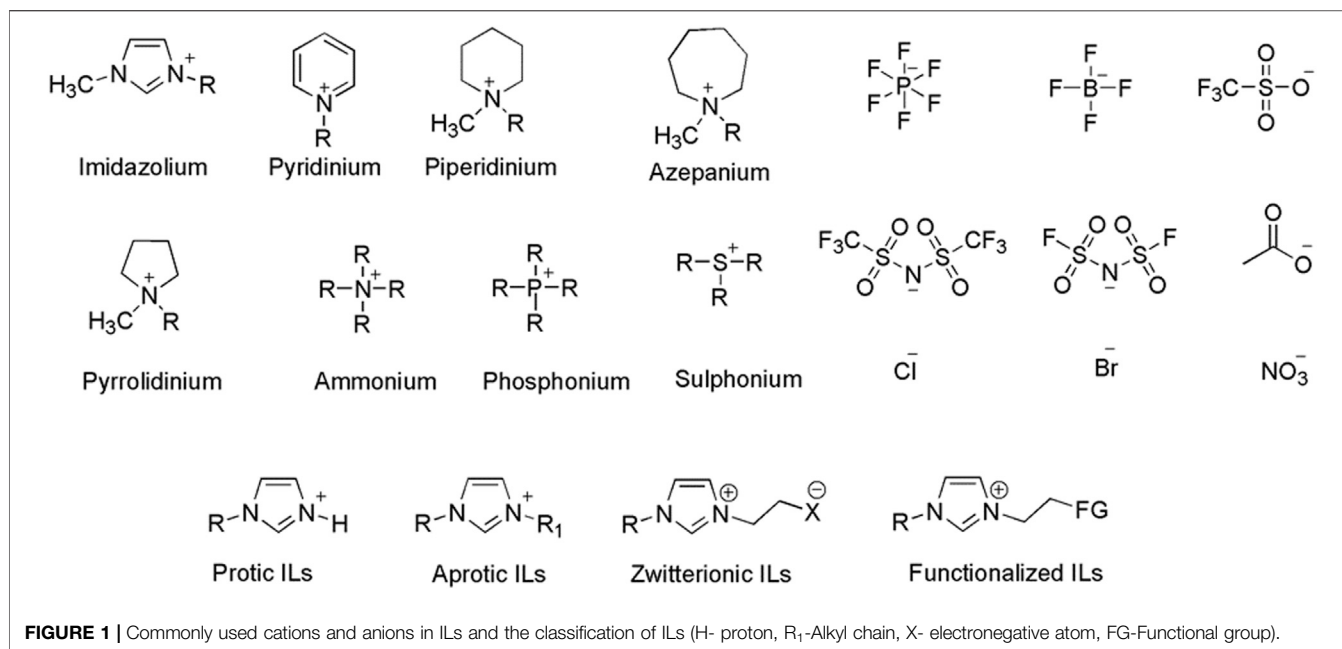
In general, the cations are large and bulky, which prevents the efficient packing of ions in the crystal lattice and results in a low melting point. The anions can be organic or inorganic, and their properties largely determine the overall characteristics of the ILs (Marsh et al., 2004; Chellappan et al., 2011; Lethesh et al., 2014b). Physicochemical and electrochemical properties of ILs can also be tuned by a meticulous selection of cation/anion pairs and by introducing desired functional groups (Davis, 2004) (Giernoth, 2010) on the ions according to requirements (Li et al., 2006; Tang et al., 2012). This flexibility makes ILs be regarded as designer solvents.

Given significant effort has been devoted to the development of ILs electrolyte for SCs (Varzi et al., 2014; Aradilla et al., 2019; Ma et al., 2018). Figure 2 summarizes the applications of SCs with IL-based electrolytes, charge storage mechanism of the pseudocapacitor and EDLC (Wang et al., 2016) and graphical representation of cyclic voltammetry (CV) curves of pseudocapacitor and EDLC (Lin Z. et al., 2011). Notwithstanding, some challenges still need to be overcome for increased/large-scale application of ILs as electrolytes for SC. Although many exciting works have reviewed the application of IL electrolyte in SC (Zhong et al., 2015; Van Aken et al., 2015; Shahzad et al., 2019; Lian C. et al., 2019), (Pan et al., 2020; Xu et al., 2021; Miao et al., 2021), a specialized review explaining the relation between IL chemistry and performance of ILs as electrolytes in SC has not received much attention. In addition, there is also a lack of clear explanations regarding the design strategies to improve transport properties and electrochemical performance of the IL electrolytes for SC. Herein, we attempt to bridge this gap with a detailed evaluation of ILs physicochemical properties and their contributions to SC performance, in addition to design considerations and challenges of applying neat ILs as electrolytes in SC. We specifically focus on neat ILs used as SC electrolytes to exclude the influence of other solvents. In neat ILs, the cation nature, the alkyl spacer length on the cation, and the type of anions playing major roles in deciding their electrochemical properties and electrolyte performance. Hence, they provide the opportunity to tune the electrolyte properties by the proper selection of cation-anion combinations. In addition, the effect of solvation can be avoided using ILs because they are made up of cations and anions. Previous studies on ILs electrolytes published from 2010 were only considered to establish a concise review. The abbreviations used in this review are given in Table 1.

## SUPERCAPACITOR PERFORMANCE WITH NEAT IONIC LIQUIDS ELECTROLYTES

### Imidazolium Based Ionic Liquids

Imidazolium-based ILs are among the most extensively studied ILs and electrolytes in SC because of their low viscosity and high



conductivity, especially when paired with a range of carbon electrodes, as seen in a recent study (Ortega et al., 2020). Where imidazolium ILs [(EMIM)(Tf<sub>2</sub>N)] and [(EMIM)(BF<sub>4</sub>)] were paired with different carbon electrode materials such as; activated carbon (AC), mesoporous carbon (MES), multi-walled carbon nanotubes (MWCNT), and reduced graphene oxide (RGO) in SC.

The study aimed to obtain insights on; compatibility of the ions with the electrodes, factors affecting the charge accumulation and, its influences on the SC performance. Interestingly, although the ILs investigated contain the same cation, their properties were entirely different. For instance, (EMIM)(Tf<sub>2</sub>N) is hydrophobic, while (EMIM)(BF<sub>4</sub>) is hydrophilic. In addition, (EMIM)(BF<sub>4</sub>)

showed higher ionic conductivity (14 mS cm<sup>-1</sup>) despite its higher viscosity (42 cP). The observations reference the role of the paired anion with imidazolium plays in the physical properties. **Figure 3A,B** shows; the specific capacitance, energy density and, power density constructed with (EMIM)(Tf<sub>2</sub>N) and (EMIM)(BF<sub>4</sub>) with the selected electrode material.

We can conclude from **Figure 3** that imidazolium-based ILs make better SC with electrode materials containing a high volume of mesopores. The increased power density was achieved with open and accessible electrode material surfaces like mesoporous carbon (Lian Y.-M. et al., 2019) and multi-walled carbon nanotubes (Zhang et al., 2018). These observations are generally valid for a wide range of SC with IL electrolytes. In

**TABLE 1** | Abbreviations used in the manuscript.

Abbreviation	Full name
AC	Activated carbon
Al(hfip) <sub>4</sub>	Aluminum hexafluoroisopropoxide
AQ-PFS	Anthraquinone- perfluorosulfonate
Azp <sub>1,4</sub>	N-butyl-N-methylazepanium
Azp <sub>1,6</sub>	N-methyl-N-hexylazepanium
B(CN) <sub>4</sub>	Tetracyanoborate
BF <sub>4</sub>	Tetrafluoroborate
BMIM	1-Butyl-3-methylimidazolium
C	Specific capacitance
cP	Centipose
C(CN) <sub>3</sub>	Tricyanomethanide
DCA	Dicyanamide
EDLC	Electric double layer capacitor
EMIM	1-Ethyl-3-methylimidazolium
FAP	Tris(pentafluoroethyl)trifluorophosphate
FSI	Bis(fluorosulfonyl)imide
Furoate	Furoate
I	Current
ILs	Ionic liquids
LUMO	Lowest unoccupied molecular orbit
MES	Mesoporous carbon
Me <sub>3</sub> S	Trimethylsulphonium
MIM	1-Methylimidazolium
MMIM <sub>202</sub>	1-(2-ethoxyethyl)-2,3-dimethylimidazolium
MWCNT	Multi-walled carbon nanotubes
N <sub>1444</sub>	Tributylmethylammonium
N <sub>222H</sub>	Triethylammonium
PILs	Protic ionic liquids
Pip <sub>1,3</sub>	N-propyl-N-methylpiperidinium
Pip <sub>1,4</sub>	N-butyl-N-methylpiperidinium
Pyr	Pyrrolidinium
Pyr <sub>1,3</sub>	N-Methyl-N-propylpyrrolidinium
Pyr <sub>1,4</sub>	N-Methyl-N-butylpyrrolidinium
Pyr <sub>1, 201</sub>	N-(2-methoxyethyl)-N-methylpyrrolidinium
P <sub>222,201</sub>	(2-methoxyethyl)trimethylphosphonium
P <sub>4444</sub>	Tetrrabutylphosphonium
RGO	Reduced graphene
SC	Supercapacitors
SCN	Thiocyanate
SeCN	Selenium thiocyanate
S <sub>221</sub>	Diethylmethylsulfonium
S <sub>222</sub>	Triethylsulfonium
S <sub>223</sub>	Diethylpropylsulfonium
TEMPO	2,2,6,6-tetramethylpiperidiny-1-oxyl
Tf <sub>2</sub> N	Bis(trifluoromethylsulfonyl)imide

carbon-based electrode materials with high pore volumes and many micropores (like activated and mesoporous carbons), the interactions between the imidazolium cations and the desorption of co-ions present in the pores govern the specific capacitance and resistance of the electrochemical double-layer capacitance. A summary of the performance of different SC containing neat imidazolium ILs electrolyte is showed in **Table 2**.

The performance (specific capacity and energy density) of the SC in **Table 2** emphasizes that matching the pore size of the electrode with the ionic size of the ILs electrolyte is not the only essential criteria in selecting carbon electrode materials for SC. Other interactions of the ILs with electrode materials, including ion-ion interaction within the ILs, functional groups on the carbon electrode surface, are among other considerations, as

will be seen in subsequent sections of this work. A feature observation that qualitatively defines a SC as an electrochemical double layer supercapacitor is the near box-like shape of the cyclic voltammetry response, which also depicts the influence of ion diffusion limitation on limiting current density. Ion diffusion limitations are often defined by electrical conductivity and prevalent electrode mesopore (Hu et al., 2019). The key is that the pore structure of the electrode creates an easy path for the electrolyte ions to access the electrode surface, as shown by Tamailarasan et al. (Tamailarasan and Ramaprabhu, 2012).

Ion diffusion limitations can also be solely a result of the IL property, the physicochemical properties of two imidazolium containing tris(pentafluoroethyl)trifluorophosphate (FAP) and tetracyanoborate  $\{[B(CN)_4]^{-}\}$  anions were evaluated, and their performance as the electrolyte in SC was studied (Seki et al., 2012) (**Table 2**). Due to the larger size of the  $(FAP)^{-}$  anion, the viscosity of  $(FAP)^{-}$  anion-based IL (43 mPa.s) was higher in comparison with  $[B(CN)_4]^{-}$  anion-based counterpart (15 mPa.s). At the same time, the ionic conductivity of (EMIM)(FAP) was almost three times lower ( $6.9 \text{ mS cm}^{-1}$ ) than (EMIM)  $[B(CN)_4]$  ( $19.0 \text{ mS cm}^{-1}$ ) at  $30^{\circ}\text{C}$ . In other words, the nature of the anions playing a significant role in determining the properties of ILs and the SC performance.

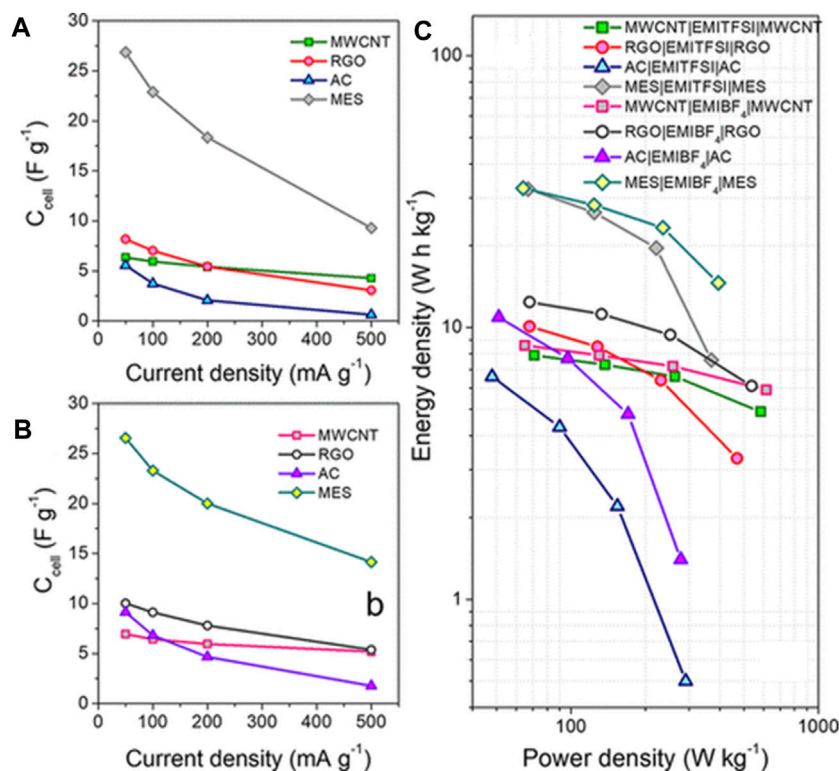
In addition to single/isolated charge-discharge response, an important performance metric for SC is capacity retention and cycling stability (Kurig et al., 2012). In investigations of the chemical reversibility of IL SC systems with (EMIM)<sup>+</sup> cation and different anions such as  $(BF_4)^{-}$ ,  $(Tf_2N)^{-}$ ,  $(FSI)^{-}$ ,  $(FPA)^{-}$ ,  $[B(CN)_4]^{-}$  and  $(SCN)^{-}$  (Kurig et al., 2011). The oxidation of the  $(SCN)^{-}$  to thiocyanogen caused deviation from the ideal capacitive behaviour. Cycling stability in SC can also be linked to the wettability of the electrolyte on the electrode pore walls due to the presence of functional groups on the pore walls (Thangavel et al., 2018).

Generally, we observed from these earlier studies that the relatively good performance of imidazolium cation based ILs as SC electrolytes might be related to small ionic size, appreciable electrochemical stability (depending on the paired anion), low viscosity, and high conductivity.

## Redox-Active Ionic Liquids Electrolytes

To further boost the energy density of SC, research efforts have been dedicated to redox-active ILs. An additional charge storage mechanism (pseudocapacitance) is offered from the redox species inherent in the ILs rather than applying pseudocapacitive solid electrode materials. SC assembled with redox-active ILs further blur the lines between batteries and SC, given the galvanostatic charge-discharge response of these SC begins to look more “battery-like”. Fic et al. (2019) took advantage of pseudo halide anion property and excellent transport properties of selenocyanate (SeCN) anion based ILs to develop a redox-active IL for SC. These ILs proved promising candidates as they were previously extensively studied in dye-sensitized solar cells (Wang et al., 2004).

An (EMIM)(SeCN) was tested as a SC electrolyte adopting an activated carbon electrode (Fic et al., 2019). Due to low viscosity



**FIGURE 3** | Specific capacitance as a function of current density for the SCs with different porous carbon electrodes and with (A) (EMIM)(Tf<sub>2</sub>N) and (B) (EMIM)(BF<sub>4</sub>) as electrolytes. Reprinted with permission from (Ortega et al., 2020), American Chemical Society.

(17 mPs) and relatively high conductivity (25 mScm<sup>-1</sup>), (EMIM)(SeCN) showed promising capacitance (Table 3), especially at higher current density (42 Fg<sup>-1</sup> at 2.5 Ag<sup>-1</sup>). The appreciable performance of the (SeCN)<sup>-</sup> anion based ILs might be related to their reasonable electrochemical stability, low viscosity, small ionic volumes, and, therefore, high ionic conductivity. Other previous research efforts applied; Cu (II) metal-containing ILs (Sun et al., 2010), bromide ion species (Br<sub>2</sub>/Br<sub>3</sub><sup>-</sup>) (Yamazaki et al., 2012), and hydroquinone (Sathyamoorthi et al., 2015).

The higher capacitance value of copper containing ILs is associated with the pseudocapacitance contribution from Cu (II)/Cu redox reaction (Table 3). Imidazolium cation can coordinate with the metals through its acidic proton on the C<sub>2</sub> carbon atom and form the Cu (II) complex of the ILs (Blue et al., 2006). It is worth noting that thermal stability and the effect of halide content on transport properties of ILs with the metal complexes are often unreported. It is known that even a minimal concentration of halide impurities can detrimentally affect the viscosity of ILs (Seddon et al., 2000). Given these concerns and SC performance targets, the optimal position and polarity of the redox-active component/molecule in the IL also need to be evaluated.

Bi-redox ILs with Anthraquinone, on anion [(AQ-PFS)<sup>-</sup>] and 2,2,6,6-tetramethylpiperidiny-1-oxyl (TEMPO) on imidazolium cation [(MIM-TEMPO)<sup>+</sup>] have also been demonstrated as electrolyte for SC (Mourad et al., 2017). The bi-redox IL

introduced had to be dissolved in (BMIM)(Tf<sub>2</sub>N) (because of high viscosity) to enable testing at room temperature. In contrast, neat bi-redox ILs electrolytes were tested at elevated temperatures (60°C) because of the significant decrease in viscosity with increasing temperature.

Applying only (BMIM)(Tf<sub>2</sub>N) electrolyte, the double-layer charge storage mechanism is seen without any Faradaic reactions. In the case of bi-redox ILs dissolved in (BMIM)(Tf<sub>2</sub>N), the redox-active ions, (AQ-PFS)<sup>-</sup> and (MIM-TEMPO)<sup>+</sup> are electro adsorbed on the surface of the carbon electrode and also undergo Faradaic reactions. The introduction of the reducible moiety on the anion and oxidizable species on the cation helped generate bi-anions and bi-cations at the anode and cathode. From the above discussion, we can conclude that the introduction of the redox active materials can improve the performance of the SC. However, it can detrimentally affect the transport properties and electrochemical stability of the ILs. The summary of the performance of the redox-active ILs is summarized in Table 3.

## Protic Ionic Liquids-Based Electrolytes

The unique feature of the protic ILs (PILs) is the presence of an acidic and liable proton (hydrogen) on the cationic core, which can involve coordinating with metals (Menne et al., 2014). However, this exchangeable hydrogen on the cationic core results in low thermal stability of PILs. Due to the relatively easy synthesis procedure and non-requirement of purification

**TABLE 2** | Summary of SC performance with imidazolium-based IL.

Entry	IL	Electrode materials	Specific capacitance (F g <sup>-1</sup> )	Specific capacitance based on	Energy density (Wh kg <sup>-1</sup> )	Ref
1	(EMIM)(Tf <sub>2</sub> N)	Activated carbon	5.57	Mass of active materials (both electrodes)	—	Ortega et al. (2020)
		Mesoporous carbon	26.86	Mass of active materials (both electrodes)	—	Ortega et al. (2020)
		Multi-walled carbon nanotubes	6.35	Mass of active materials (both electrodes)	—	Ortega et al. (2020)
		Reduced graphene oxide	8.18	Mass of active materials (both electrodes)	—	Ortega et al. (2020)
		Graphene	332	—	156	Li et al. (2016a)
		Carbon nanotube	201	Mass of active materials (one electrode)	171	Tamailarasan and Ramaprabhu, (2012)
2	(EMMIM)(Tf <sub>2</sub> N)	Activated carbon	41.7	Mass of electrodes	42.3	Sillars et al. (2012)
3	(EMIM)(BF <sub>4</sub> )	Activated carbon	9.15	Mass of active materials (both electrodes)	—	Ortega et al. (2020)
		Mesoporous carbon	26.57	Mass of active materials (both electrodes)	—	Ortega et al. (2020)
		Multi-walled carbon nanotubes	6.96	Mass of active materials (both electrodes)	—	Ortega et al. (2020)
		Reduced graphene oxide	10.02	Mass of active materials (both electrodes)	—	Ortega et al. (2020)
		Graphene oxide	144.4	Mass of active materials (both electrodes)	174	Lei et al. (2013)
		Mesoporous graphene	250	Mass of electrode (both electrodes)	85.6	Liu et al. (2010)
		Activated carbon fiber	204	Mass of active materials (one electrode)	113	Hu et al. (2019)
		Graphene nanofiber	192	Mass of active materials (one electrode)	112	Hu et al. (2019)
		Activated carbon	143	Mass of active materials (one electrode)	110	Hu et al. (2019)
		Carbon cloth	125	Mass of single electrode	44	Kurig et al. (2011)
		Graphene aerogel	203	Mass of single electrode	100.7	Chen et al. (2018)
		Graphene	174	—	81	Li et al. (2016a)
		Activated carbon	56	Mass of electrodes (both electrodes)	70	Sillars et al. (2012)
		Porous carbon	180	Mass of electrodes (both electrodes)	80	Tran et al. (2015)
4	(EMIM)(FAP)	Carbon nanotube	183.3	Mass of single electrode	80	Shao et al. (2015)
		Carbon	28.3	Mass of electrodes (both electrodes)	—	Seki et al. (2012)
5	(EMIM)(TCB)	Carbon	29.6	Mass of electrodes (both electrodes)	—	Seki et al. (2012)
6	(EMIM)(BF <sub>4</sub> )	Carbon	313	Mass of active materials (both electrodes)	174	Thangavel et al. (2018)
7	(BMIM)(SCN)	ZnFe <sub>2</sub> O <sub>4</sub>	781	Mass of active materials (one electrode)	156	Vadiyar et al. (2015)
8	(EMIM)(SCN)	ZnFe <sub>2</sub> O <sub>4</sub>	590	Mass of active materials (one electrode)	78	Vadiyar et al. (2015)
9	(EMIM)[B(CN) <sub>4</sub> ]	Carbon cloth	140	Mass of single electrode	49	Kurig et al. (2011)
10	(MIM)(SCN)	ZnFe <sub>2</sub> O <sub>4</sub>	250	Mass of active materials (one electrode)	50	Vadiyar et al. (2015)
11	(EMIM)[N(CN) <sub>2</sub> ]	Activated carbon	10.7	Mass of electrode	18.2	Sillars et al. (2012)

steps, protic ILs receive much attention in various applications such as; electrolyte for lithium-ion rechargeable batteries (Menne et al., 2013; Vogl et al., 2014), extraction processes (Wang et al., 2020; Rodrigues et al., 2018; Janssen et al., 2016).

In a recent study (Mayrand-Provencher and Rochefort, 2009), PILs were prepared from aromatic heterocyclic compounds (base) containing two nitrogen atoms and trifluoroacetic acid.

The effect of multiple proton exchange sites and the impact of the acid strength (pKa) on the physicochemical properties of these PILs and the capacitance of SC containing RuO<sub>2</sub> electrodes were evaluated. At the same time, specific conductivities recorded varied from 0.71 to 9.07 mScm<sup>-1</sup> at 27°C. In all the PILs studied, conductivity improved with the amount of acid used, and the highest value was obtained in a base and acid ratio of 1:2.

**TABLE 3** | Summary of SC performance of redox-active ILs.

Entry	ILs	Electrode	Specific capacitance (F g <sup>-1</sup> )	Specific capacitance based on	Energy density (Wh kg <sup>-1</sup> )	Ref
1	(EMIM)(SeCN)	Activated Carbon	42	Mass of active materials (both electrodes)	—	Fic et al. (2019)
2	(EMIM)(BF <sub>4</sub> )/Cu(II)	Porous Carbon	225	Mass of active material (one electrode)	45	Sun et al. (2010)
3	(N <sub>222,H</sub> )(Tf <sub>2</sub> N)	Activated Charcoal	72	Mass of active material	31.22	Sathyamoorthi et al. (2015)
4	(MIM-TEMPO) (AQ-PFS)	PICA	200	Mass of one electrode	50	Mourad et al. (2017)
5	[(EMIM)Br]/ (EMIM)(BF <sub>4</sub> )	Activated carbon fiber clothes	59	Mass of electrodes (both electrodes)	—	Yamazaki et al. (2012)

This increase in conductivity is related to the decrease in the viscosity obtained at that ratio.

As expected with PILs, the pH (potential of hydrogen) of the resulting SC electrolyte has a significant influence on the specific capacitance value, as demonstrated by Demarconnay and co-workers (Demarconnay et al., 2013). PILs such as pyrrolidinium nitrate [(Pyr)(NO<sub>3</sub>)] and triethylammonium bis(trifluoromethylsulfonyl)imide [(N<sub>222H</sub>)(Tf<sub>2</sub>N)] with high conductivity, varying pH, and water content were employed as electrolytes with carbon-based electrodes. Varying pH of the electrolyte from 7 to 11 increased the specific capacitance from 121 to 208 Fg<sup>-1</sup> for (Pyr)(NO<sub>3</sub>). The higher capacitance value at pH11 was attributed to the pseudocapacitive contribution arisen due to the increased mobility of PILs proton by the presence of multiple amine sites on the electrode material. The water content in the electrolyte detrimentally affected the operating voltage and specific capacitance value. Considering the difficulty in drying the PILs, care must be taken when selecting the anions of the PILs. The PILs containing hydrophobic anions tend to reduce the water content in the PILs and can contribute to enhanced performance.

In summary, PILs demonstrated so far in the literature are promising candidates for carbon electrode SCs because of the pseudo-faradaic reaction between the oxygen-containing functional groups on the activated carbon and the proton on the PILs. The low operating temperature some PILs offer (Montes-Morán et al., 2004) might be valuable in various applications like aerospace.

### Sulfonium Based Ionic Liquids Electrolyte

Like PILs, sulfonium-based ILs are also relatively easy to synthesize for application as SC electrolytes, as shown by Anouti et al. (2012). They synthesized trimethylsulphonium bis(trifluoromethylsulfonyl)imide (Me<sub>3</sub>S)(Tf<sub>2</sub>N) by the simple alkylation of dimethylsulfide with corresponding alkyl halides, followed by a metathesis reaction of the resulting halide salt with Li (Tf<sub>2</sub>N). Although the (Me<sub>3</sub>S)(Tf<sub>2</sub>N) was obtained as solid at room temperature (T<sub>m</sub> = 45.5°C), the IL reported high conductivity (20.42 mS cm<sup>-1</sup>) at 80°C, which is significantly higher than the ammonium-based ILs used in SC applications. (Me<sub>3</sub>S)(Tf<sub>2</sub>N) also showed very low viscosity (3 mPas) at similar experimental conditions. The smaller ionic size and high fluidity

at 80°C promoted the high conductivity in (Me<sub>3</sub>S)(Tf<sub>2</sub>N) ILs, typical for the ILs containing sulfonium cation. When neat (Me<sub>3</sub>S)(Tf<sub>2</sub>N) was applied as SC electrolyte (Maton et al., 2013), a potential window of 5.3V (vs. Ag/Ag<sup>+</sup>) was reported at 50°C with a capacitance value of 130 Fg<sup>-1</sup> and 140 Fg<sup>-1</sup> at 50°C and 80°C, respectively. These values are almost double that of (Pyr<sub>1,4</sub>)(Tf<sub>2</sub>N) at similar conditions with the same activated carbon electrodes.

The observed results with (Me<sub>3</sub>S)(Tf<sub>2</sub>N) reinforce the influence of high conductivity, lower viscosity, and small size of the (Me<sub>3</sub>S)<sup>+</sup>(0.6 nm) cation compared with the (Pyr<sub>1,4</sub>)<sup>+</sup>(1.1 nm) cation. The higher energy and power densities recorded for the sulfonium ILs make them a promising electrolyte class for SCs. However, the thermal stability of sulfonium-based ILs is still a concern at elevated temperatures (Zhang et al., 2009; Coadou et al., 2016).

Sampaio and co-workers also (Sampaio et al., 2019) conducted molecular dynamics studies to evaluate the electrical, dynamical and structural properties of three sulfonium based ILs diethylmethylsulfonium bis(trifluoromethylsulfonyl)imide [(S<sub>221</sub>)(Tf<sub>2</sub>N)], triethylsulfonium bis(trifluoromethylsulfonyl)imide [(S<sub>222</sub>)(Tf<sub>2</sub>N)] and diethylpropylsulfonium bis(trifluoromethylsulfonyl)imide[(S<sub>223</sub>)(Tf<sub>2</sub>N)] at atomic level. It was observed that both viscosity and ionic conductivity of these ILs varied according to cation size. However, the differences in the properties had a negligible effect on the performance of the SC, especially on the specific capacitance value, which is contradictory to the earlier reports (Li S. et al., 2016) and our previously highlighted relationships. We suspect the near uniformity of their SC-specific capacitance is due to microporous activated carbon as the electrode material, which has a smaller pore size than the ionic size of the ions in the ILs. Although the easy synthesis and favourable transport properties of sulfonium-based ILs make them suitable candidates for SC electrolytes, design protocols to improve their thermal stability are necessary for their use in high-temperature supercapacitors.

### Azepanium Based Ionic Liquids

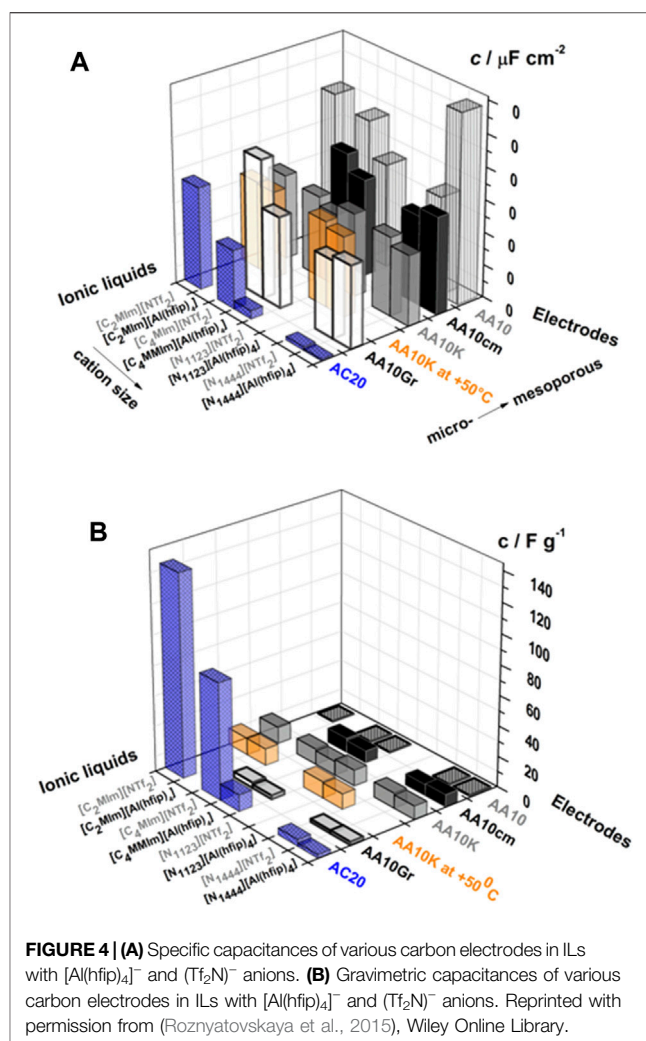
Most ILs used as electrolytes for SCs are based on aromatic or non-aromatic five/six -membered rings (imidazolium, pyrrolidinium or piperidinium). ILs with seven-membered ring (Azepanium) are also applicable and were synthesized, with their

physicochemical and electrolyte performance in SC was compared with the established (Pyr<sub>1,4</sub>)(Tf<sub>2</sub>N) electrolyte in a previous study (Pohlmann et al., 2015). The presented azepanium based ILs (N-butyl-N-methylazepanium bis(trifluoromethanesulfonyl)imide [(Azp<sub>1,4</sub>)(Tf<sub>2</sub>N)] and N-methyl-N-hexylazepanium bis(trifluoromethanesulfonyl)imide [(Azp<sub>1,6</sub>)(Tf<sub>2</sub>N)] displayed higher viscosity and lower conductivity compared to their pyrrolidinium analogues. This observation is possibly due to the larger ring size of the azepanium cation. However, the azepanium based ILs showed comparable thermal stability (>350°C) as pyrrolidinium ILs. The determination of the maximum operating voltage showed that the positive potential limit was not affected by the ILs structure. On the other hand, the negative potential limit was influenced by the size of the cation. The inferior performance of the azepanium based ILs as an electrolyte compared with the pyrrolidinium analogue was related to their high viscosity and lower conductivity. Nevertheless, considering the lower cost of azepanium ILs, modifications to reduce their viscosity and improve the ionic conductivity can transform them into electrolytes of choice in SCs.

## Functionalized Ionic Liquids

The performance of ILs based electrolytes in SC can be improved by the cautious design of ILs, including introducing functional groups to conventional ILs. Modifying the IL cations by grafting the alkyl side chain with heteroatoms (Oxygen, Nitrogen, Sulphur, etc.) can dramatically improve the ionic transport properties. The heteroatom on the alkyl chain can alter the electronic distribution of the cationic core, which will improve ionic transport properties and enhance electrochemical performance. Rennie et al. (2013), tethered oxygen atom on the alkyl side chain (ether functionalization) of the imidazolium cation [1-(2-ethoxyethyl)-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide], (MMIM<sub>202</sub> [(Tf<sub>2</sub>N)] and phosphonium cation (2-methoxyethyl) trimethylphosphonium bis(trifluoromethylsulfonyl)imide, [(P<sub>222,201</sub>)(Tf<sub>2</sub>N)]], which significantly improved the specific capacitance and reduced the resistance of a SC containing mesoporous carbon electrode. The presence of the ether group reduced the viscosity of the IL. A similar trend was observed for ILs containing other cationic cores under investigation for viscosity and thermal stability. Electrochemical impedance spectroscopy results of ILs showed significant deviation from the ideal behaviour due to the inhomogeneity on the electric double layer formed, which is typically prominent in viscous ILs with low conductivity. The improved performance of the ether group-containing ILs might be related to the presence of an electronegative oxygen atom, which might create a remote electronegative region on the cationic core and facilitated the creation of a denser double layer on the electrode surface and resulted in the displacement of a large amount of charge on the electrode.

A comparative study of electrochemical performance of ILs based on two weakly coordinating anions aluminum hexafluoroisopropoxilate {[Al(hfip)<sub>4</sub>]<sup>-</sup>} and (Tf<sub>2</sub>N)<sup>-</sup> was also performed in a SC (Roznyatovskaya et al., 2015). The



**FIGURE 4 | (A)** Specific capacitances of various carbon electrodes in ILs with [Al(hfip)<sub>4</sub>]<sup>-</sup> and (Tf<sub>2</sub>N)<sup>-</sup> anions. **(B)** Gravimetric capacitances of various carbon electrodes in ILs with [Al(hfip)<sub>4</sub>]<sup>-</sup> and (Tf<sub>2</sub>N)<sup>-</sup> anions. Reprinted with permission from (Roznyatovskaya et al., 2015), Wiley Online Library.

[Al(hfip)<sub>4</sub>]<sup>-</sup> anion showed less electrode interaction and improved transport properties compared to (Tf<sub>2</sub>N)<sup>-</sup> anion, when both were evaluated with carbon electrodes possessing micro to macropores—to study the effect of pore size-ion size matching (sieving effect) on capacitance behaviour. Both areal and specific capacitance values with cells combining electrodes with different pore sizes and ILs are shown in **Figure 4**. The sieving effect is clear in the case of electrodes with micropores. ILs with larger cation [(N<sub>1,444</sub>)<sup>+</sup>] and anions {[Al(hfip)<sub>4</sub>]<sup>-</sup>} displayed lower capacitance value. The larger size of the {[Al(hfip)<sub>4</sub>]<sup>-</sup>} anion (1.166 nm) is not able to pass through the microporous carbon electrode with an average pore size of 0.86 nm - resulting in lower capacitance than {(Tf<sub>2</sub>N)<sup>-</sup>} anion. Conversely, there was no significant difference in the capacitance for ILs with mesoporous carbon electrodes with larger pores as expected.

## Pyrrolidinium and Piperidinium Ionic Liquids

ILs with pyrrolidinium cations having simple alkyl group [(Pyr<sub>1,3</sub>)<sup>+</sup>, (Pyr<sub>1,4</sub>)<sup>+</sup>] and ether groups [(Pyr<sub>1,201</sub>)<sup>+</sup>] paired with dicyanamide (DCA) anion have been reported as electrolytes in SCs with an activated carbon-based composite electrode (Wolff



**TABLE 4** | Summary of SC performance of pyrrolidinium and piperidinium ILs.

Entry	ILs	Electrode	Specific capacitance (F g <sup>-1</sup> )	Specific capacitance based on	Energy density (Wh kg <sup>-1</sup> )	Ref
1	(Pyr <sub>1,4</sub> )[C(CN) <sub>3</sub> ]	Activated carbon	27.3	Active mass of electrodes (both electrodes)	4.5	Martins et al. (2017)
2	(Pip <sub>1,4</sub> )[C(CN) <sub>3</sub> ]	Activated carbon	17.7	Active mass of electrodes (both electrodes)	0.9	Martins et al. (2017)
3	(Pyr <sub>1,4</sub> )[B(CN) <sub>4</sub> ]	Activated carbon	20	Active mass of electrodes (both electrodes)	6	Martins et al. (2018)
4	(Pip <sub>1,4</sub> )[B(CN) <sub>4</sub> ]	Activated carbon	14.8	Active mass of electrodes (both electrodes)	1	Martins et al. (2018)
5	(Pyr <sub>1,4</sub> )(FAP)	Carbon	16.7	Mass of electrode	14.5	Sillars et al. (2012)
6	(N <sub>2224</sub> )[N(CN) <sub>2</sub> ]	Graphene	42	Mass of active materials (one electrode)	55	Zarrougui et al. (2018)
7	(N <sub>222-Propargyl</sub> )[N(CN) <sub>2</sub> ]	Graphene	55	Mass of active materials (one electrode)	49	Zarrougui et al. (2018)

et al., 2015). It was previously observed that dicyanamide anion based ILs are typically electrochemically less stable than their (Tf<sub>2</sub>N)<sup>-</sup> analogues (Zarrougui et al., 2018). Nevertheless, their high conductivity makes them a good candidate for SC electrolytes. **Table 4** shows the SC performance of some reported Pyrrolidinium and Piperidinium ILs.

Both pyrrolidinium and piperidinium cationic cores have also been investigated for SC electrolytes in combination with tricyanomethanide {[C(CN)<sub>3</sub>]<sup>-</sup>} and Tetracyanoborate [B(CN)<sub>4</sub>]<sup>-</sup> anions (Martins et al., 2017; Martins et al., 2018). It was observed that the ILs with pyrrolidinium and tricyanomethanide combinations showed similar viscosity at 25°C, while (Pip<sub>1,4</sub>)[C(CN)<sub>3</sub>] and (Pip<sub>1,4</sub>)[B(CN)<sub>4</sub>] had significantly higher viscosities due to relatively larger cation size. Consequently, pyrrolidinium-based ILs show better performance as SC electrolytes than the piperidinium counterpart (**Table 3**), which showed a significant iR drop during discharge. The effect of pyrrolidinium ion size on resulting higher viscosity electrolytes like (Pyr<sub>1,4</sub>)(FAP) was also demonstrated (Sillars et al., 2012) on the capacitance of SC applying carbon electrodes. It was observed that the higher viscosity leads to the weakening of the interaction between the electrode and electrolyte ions. From the above discussion, it is clear that the viscosity of ILs playing a significant role in determining the supercapacitor performance, which must be considered while designing new ILs electrolytes for SC.

## Other Ionic Liquids Electrolytes Systems

More ILs have been recently developed and studied in electrochemical energy storage applications like SC. An example is ILs derived from dimethylformamide (DMF) type cation, and tetrafluoroborate anion, (EDMF)(BF<sub>4</sub>) prepared and studied as a potential high-capacitance electrolyte for SC by Chen and co-workers (Chen et al., 2019). The moderate size and quasi-linear nature of the (EDMF)<sup>+</sup> cation increased ion mobility and helped the formation of a compact electric double layer resulting in better performance of the SC with (DMF)(BF<sub>4</sub>) electrolyte.

Most ILs applied as electrolytes in SC contain fluorine in the anions. A recent study (Khan and Shah, 2020) synthesized an IL with a non-fluorinated Furoate anion, in combination with tetrabutylphosphonium furoate [(P<sub>4444</sub>)(FuA)], and tested it as an electrolyte for a SCs. The advantage with some of these developed 'non-conventional' ILs is that high ionic conductivities and operating potential windows in SC applications can be reported, comparable to the most applied

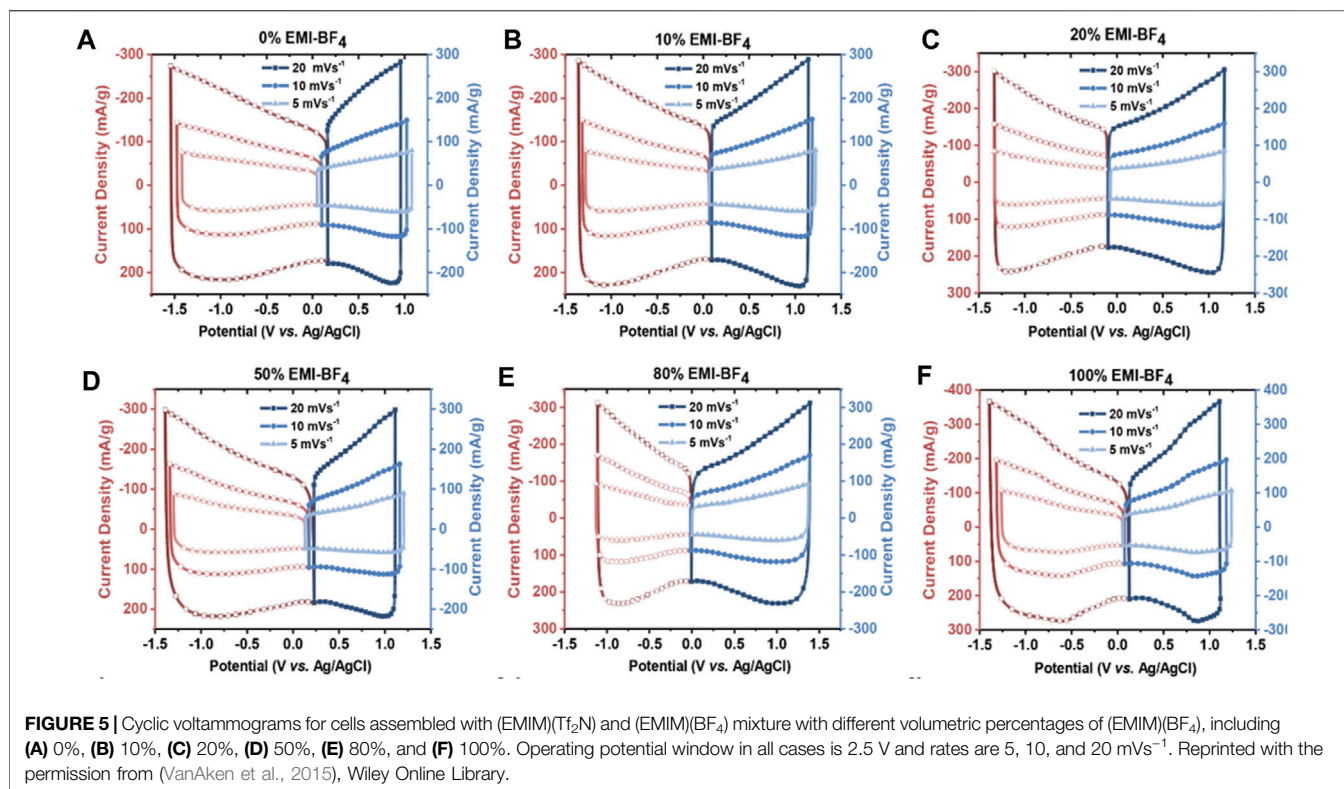
high performing ILs like (EMIM)(BF<sub>4</sub>). In addition, their synthesis can be simplified. However, there are still setbacks with the newly developed ILs in thermal stability. For example; the Furoate anion based ILs like previously mentioned (P<sub>4444</sub>)(FuA), are thermally less stable (<250 °C) in comparison to their fluorinated analogues, which is not surprising because carboxyl groups can easily undergo decarboxylation at elevated temperatures (Clough et al., 2013; Cao and Mu, 2014). Nevertheless, this report opened the possibility of developing high performing ILs electrolytes by avoiding fluorinated anions.

The mixing of two neat ILs created a new electrolyte that behaved differently than the constituent ILs as seen in the study highlighted in **Figure 5** (Van Aken et al., 2015). The use of such IL mixtures can potentially result in electrolytes with balanced charge storage, high potential window, and high energy density (Van Aken et al., 2015).

Another study (Lin R. et al., 2011) explored IL mixtures by mixing two ILs with the same anion bis(fluorosulfonyl)imide [(FSI)<sup>-</sup>], with similar cations [(Pyr<sub>1,3</sub>)<sup>+</sup> and (Pip<sub>1,3</sub>)<sup>+</sup>], which prevented ordered arrangement of the ions in the crystal lattice to avoid crystallization. The result was a new IL with a broader liquid range compared to the constituent ILs. Mixing of the two ILs extended the liquid range of the newly formed mixture to as low as -50°C, resulting in the capability to operate a SC with extended operating temperature from -50 to 100°C.

As suggested so far, the electrochemical performance of these non-conventional ILs is defined by their molecular structure. Therefore, the structure-performance influence is always worthy of investigation. Mousavi et al. (2016) reported the effect of ILs structure on the physical properties, electrochemical stability, capacitance, and specific energy when applied as electrolytes in SC using carbon electrodes with uniform and highly interconnected mesopores. ILs containing different anions (tetrafluoroborate, trifluoromethanesulfonate, trifluoromethanesulfonimide and most used cations (imidazolium, ammonium, pyridinium, piperidinium, and pyrrolidinium) were selected for the study seen in **Figure 6**.

The electrochemical stability measurements of the ILs showed that anions have little effect on the cathodic stability of these ILs. On the other hand, the cation has a significant influence on the anodic limit of the ILs. Quaternary ammonium ILs showed the highest anodic stability compared to their aromatic counterparts. Given cation structure substantially impacts the cathodic stability of the ILs, non-aromatic quaternary ammonium cationic cores displayed better stability than their aromatic analogues. The



reason is that cations with lower LUMO (lowest unoccupied molecular orbital) energy levels are prone to reduction. The investigators observed that alkyl spacer lengths on the cations had no significant influence on the electrochemical stability of the ILs. Cation size also had a considerable effect on the viscosity and conductivity of the electrolyte and the capacitance of assembled SC. In the study (Mousavi et al., 2016), imidazolium and pyridinium-based ILs provided the highest cell capacitance, and ammonium-based ILs offer potential windows much larger than imidazolium and pyridinium ILs. Although alkyl chain lengths on the imidazolium cation did not influence their electrochemical potential window, it significantly influenced the specific capacitance of SCs with imidazolium ILs (Figure 6).

The increase in the alkyl chain length on the imidazolium cation (larger cation) decreased the gravimetric specific capacitance due to the decrease in the concentration of the counterions in the electrode pores due to the sieving effect of the electrolyte. In addition, the increased ionic size also reduces the accessible surface area. (EMIM)(Tf<sub>2</sub>N) displayed the highest capacitance among the imidazolium ILs studied (Mousavi et al., 2016). This study clearly shows that the size of the ILs ions should be considered when selecting electrode materials for ILs based supercapacitors.

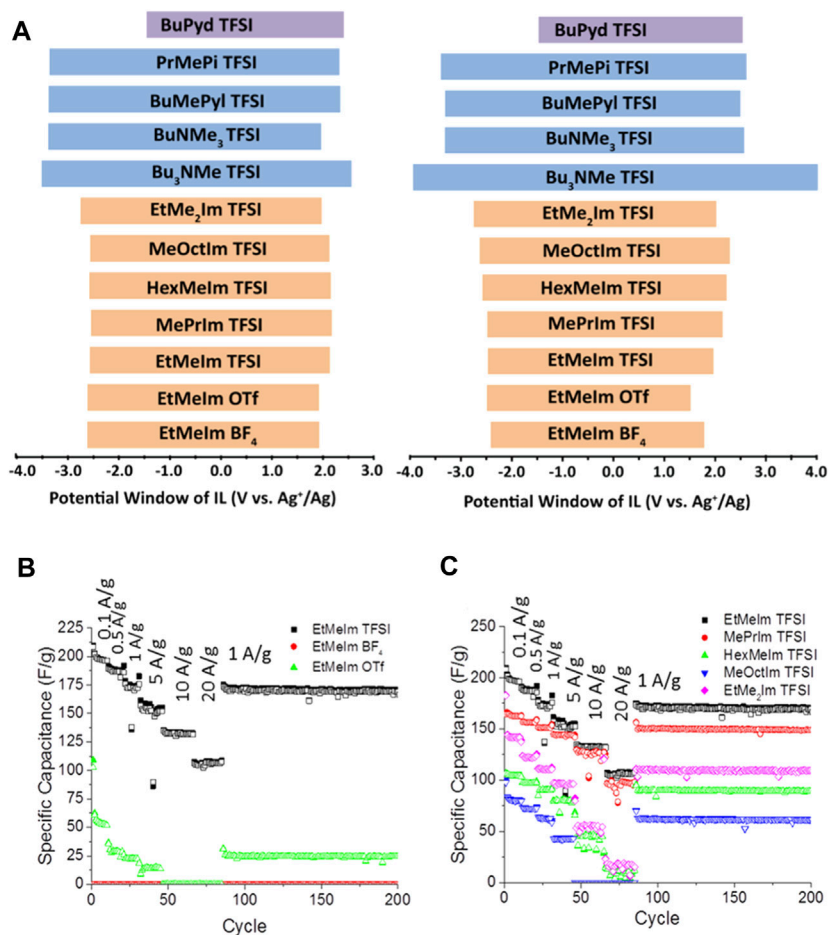
## DESIGN STRATEGIES FOR IONIC LIQUIDS ELECTROLYTE FOR SUPERCAPACITORS

ILs have some advantages over conventional organic and aqueous electrolytes for SC. However, ILs suffer some setbacks such as

high viscosity, low ionic conductivity, and low degree of ion dissociation—resulting in SC with lower power than other electrolytes. From our discussions on different IL structures, resulting IL physicochemical properties, and their IL–electrode interactions in SCs, we propose different design strategies applied to IL development to improve their SC performance.

One of the methods to increase ionic conductivity by decreasing viscosity of the ILs is through the introduction of functional groups such as ether groups on the cationic core of the ILs (Chen et al., 2012; Raj et al., 2018; Raj et al., 2017; Chen et al., 2016; Jin et al., 2012). The introduction of these functional groups on the cation can modify the electronic environment of the ILs due to their highly flexible nature, which increases their free volume and results in a lower viscosity (Chen et al., 2012). Another strategy to reduce the viscosity of the ILs is creating asymmetry in the cation by attaching alkyl substitution in the relevant positions of the cationic core. For instance, the viscosity of the pyridinium-based ILs, as previously discussed, can be significantly improved by attaching alkyl groups on the meta (3) position of the pyridine ring (Lethesh et al., 2019; Chellappan et al., 2011).

Anions play a crucial role in determining the overall electrochemical properties of ILs. Viscosity, conductivity, thermal stability, and hydrophobicity of the ILs can be tuned with the selection of relevant anions with delocalized charge or weak coordination (Timofte and Mudring, 2006). It is worth noting that although non-coordinating anions can reduce the viscosity and increase the conductivity of ILs, these anions can also detrimentally affect the operating potential of ILs (Pandey



**FIGURE 6 |** effect of; (A) alkyl chain length on the electrochemical stability window, (B) anion, (C) alkyl spacer length on the specific capacitance values at various rates for mesoporous carbon electrodes using the IL electrolytes. Reprinted with permission from (Mousavi et al., 2016), American Chemical society.

and Hashmi, 2013). Pairing cations with smaller size anions have conflicting effects. Smaller ions can increase the conductivity of ILs because of their higher intrinsic mobility (Tsuzuki et al., 2005; Yoshida et al., 2007). Conversely, smaller ions can also result in increased ion-ion Coulombic interactions resulting in high viscosity. Hence, an optimum ion size pairing is sought to maximize conductivity and minimize the viscosity of resulting IL.

Improving the electrochemical stability of ILs can be done by introducing modifications to the cationic core of the ILs. It is known that quaternary ammonium ILs undergo decomposition primarily through Hoffman elimination by utilizing the hydrogen atoms on their  $\beta$ -position (DeVos et al., 2014; Lethesh et al., 2014a). The replacement of the  $\beta$ -hydrogens can limit the Hoffman elimination reaction rate and significantly improve the electrochemical potential window of ILs. However, it is worth noting that the replacement of the  $\beta$ -hydrogens might affect other physicochemical properties (depending on the nature of the substituents) of the ILs. Hence, care must be taken while selecting the substituents on the  $\beta$  position of the quaternary ammonium ILs. As discussed earlier, phosphonium cations can increase the electrochemical stability and operating potential

window of SC (Khan and Shah, 2020). The use of tetraalkylphosphonium cations can also increase the electrochemical stability window of ILs because of their unique electrochemical decomposition mechanism (Bradaric et al., 2003). However, higher viscosity of the phosphonium based ILs must be taken into account while employing them as an electrolyte in SC (Del Sesto et al., 2005).

Organic solvent additives or mixtures with ILs can also optimize the ILs electrolytes for SC applications. Although IL-organic solvent mixture electrolytes improve capacitance compared with the neat ILs system (Lian et al., 2016; Siinor et al., 2013), energy density is sometimes compromised when the mixture results in a narrower potential window. Therefore, adding organic solvents with good conductivity and high anodic stability is expected to improve both capacitance and energy density in IL-organic solvent mixture electrolyte systems. Furthermore, even when a high electrochemical potential window ILs are applied in a SC, the IL may not be fully utilized in both electrodes of the SC when there is an asymmetry in the capacitance of the anode and cathode. This imbalance can result in electrolyte decomposition and can be remedied to

achieve high cell voltage by mixing two suitable ILs instead of an IL-organic solvent mixture.

## CONCLUSION AND FUTURE PERSPECTIVE

This work sought to provide an outlook on the prospects of neat ionic liquids (ILs) as supercapacitor (SC) electrolytes. We specifically focus on IL–SC electrolyte design considerations from our observations and reported conclusions in previous works towards the performance of neat ILs in SCs.

The chemistry of charge storage reactions involved in different classes of ILs electrolyte was explained in detail before we provided design strategies for new IL electrolyte systems for SCs. The role of ILs physicochemical properties such as viscosity, ionic conductivity, ionic size, thermal stability, electrochemical stability (potential window) on the performance of the SC—in terms of specific capacitance, energy density was discussed. In addition, we also highlighted plausible mechanisms of IL cycling stability when paired with typical carbon-based electrode materials in SC.

The effect of ILs structure and the impact of distinct functional groups on their physicochemical properties were provided in detail. Although notable accomplishments were made in ILs electrolytes for SCs, many challenges are yet to be addressed in the commercialization of SC with ILs electrolytes. A practical method for widening the operating potential window and operating temperature range of the IL-based electrolytes is yet to be established. We found there is a lack of clear understanding about the electrochemical degradation mechanism of the ILs electrolyte in SC, which is a significant roadblock in designing new ILs with a wide operating potential window.

We suggest more effort is required both experimentally and theoretically to establish the relation between ILs transport and thermal properties with respect to its molecular structure, which will help to design promising ILs electrolytes for electrochemical energy storage devices. More studies are also required towards the standardization of the electrochemical characterization methods for IL electrolytes.

Formulation of electrolytes with a wide electrochemical stability window is essential for developing high-performance SC, and ILs displayed massive potential in this regard. Although ILs can widen the operating potential of the SC devices, the design of ILs suitable for different operating conditions is essential to utilize their full potential. For instance, ILs with promising transport properties at sub-zero temperature and ILs with long-term thermal stability of more than 200°C are not

available. Hence, it is necessary to focus on developing ILs to operate in different experimental conditions. Another exciting research direction will be creating a suitable method for identifying the best electrode - ILs combination because the literature data confirmed that the electrode structure could influence the arrangement of ILs at the interface. The technique will help to improve the capacitance of the SC without sacrificing the power and energy density. The commonly used ILs as an electrolyte in SC have moderate to high toxicity, and they are not readily biodegradable. The use of such toxic ILs in a commercial scale can cause environmental and health issues. Hence, it is vital to develop non-toxic and readily biodegradable ILs without compromising their electrochemical and transport properties in large-scale electrochemical applications.

Despite the unique advantages of ILs electrolytes, their cost and purification issues are major concerns while using them in commercial applications. The development of a simple post-synthesis purification step (or no purification step) and the use of low-cost raw materials need to be explored to make ILs a cheaper alternative to organic-based electrolytes. The purification of ILs is critical because even a trace amount of impurities (water/halide) decreases the operating potential window and increases self-discharge. Due to the enormous increase in the demand for wearable devices, the “ionogel” electrolyte (neat ILs with polymer skeleton) might be the future of IL-based electrolytes, providing adequate mechanical stability improvements. Ionogels can provide flexible SCs with superior capability because of their high ion conductivity and fast ion diffusion. There are emerging reports of polymerized ILs based solid electrolytes for SC. We believe these electrolytes will continue to be promising because their appreciable conductivity often comes with notable electrochemical stability.

## AUTHOR CONTRIBUTIONS

The idea of this review paper was conceived by KL. KL wrote the manuscript with significant contributions from MB and RS. All authors have read and approved the final version of the manuscript.

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**Conflict of Interest:** KL, MB, and RS were employed by the company Dubai Electricity and Water Authority (DEWA).

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