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Ionic Liquids/Ionic Liquid Crystals for Safe and Sustainable Energy Storage Systems

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Abstract

Ionic liquid crystals are organic salts having synergistic properties of ionic liquids and liquid crystalline materials endowed with non-covalently bound delocalised ion pairs of large organic cations and anions. They can undergo stimulus-responsive anisotropic phase change, followed by enhancement in ionic diffusion and conductivity, which makes them ideal candidates as electrolyte in energy storage systems. Our goal in this chapter is to survey the key developments in the field of ionic liquid crystalline electrolytes and to generate curiosity in the wider research community in tackling challenges in the electrolyte materials for sustainable energy related devices, such as supercapacitors, Li batteries, fuel cells and dye-sensitized solar cells (DSSCs).

Keywords: ionic liquids, ionic liquid crystals, energy storage, supercapacitors, batteries

1. Introduction

Research and development, in the arena of sustainable energy, is receiving overwhelming interest due to the rapid proliferation of portable nano-electronic devices and also evolution in lifestyle. Due to the depletion of petroleum-based energy resources, researchers are turning towards the energy production from wind, solar, tidal, hydro and geothermal energy sources. But these resources are intermittent with time and season. Safe, sustainable and clean strategies for energy storage, such as supercapacitors, batteries, fuel cells, etc. have been explored tremendously in recent years to store energy in a sustainable way. Electrodes and electrolytes are the main components present in the energy storage devices. Electrolytes are the materials through which the transport of ions takes place from anode to cathode and vice versa, during charge-discharge processes. Transport and diffusion of ions through the electrolyte are largely influenced by various material parameters, such as viscosity, porosity and ionic conductivity

of the electrolytes. Among the presently used liquid electrolytes, ionic liquids (ILs) are delivering excellent performance due to their high ionic conductivity, wide electrochemical stability window, good thermal stability, wide liquidity range, non-volatility and non-toxicity. Being composed of ion pairs bound by non-covalent interactions, they are bestowed with innumerable fascinating properties suitable for various applications [1, 2]. Generally, ionic liquids contain the cationic centres, such as nitrogen, oxygen, sulphur, phosphorous atoms and counter anions, such as halides, hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-), bis-triflimide $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$, etc. as shown in **Figure 1** [3–10].

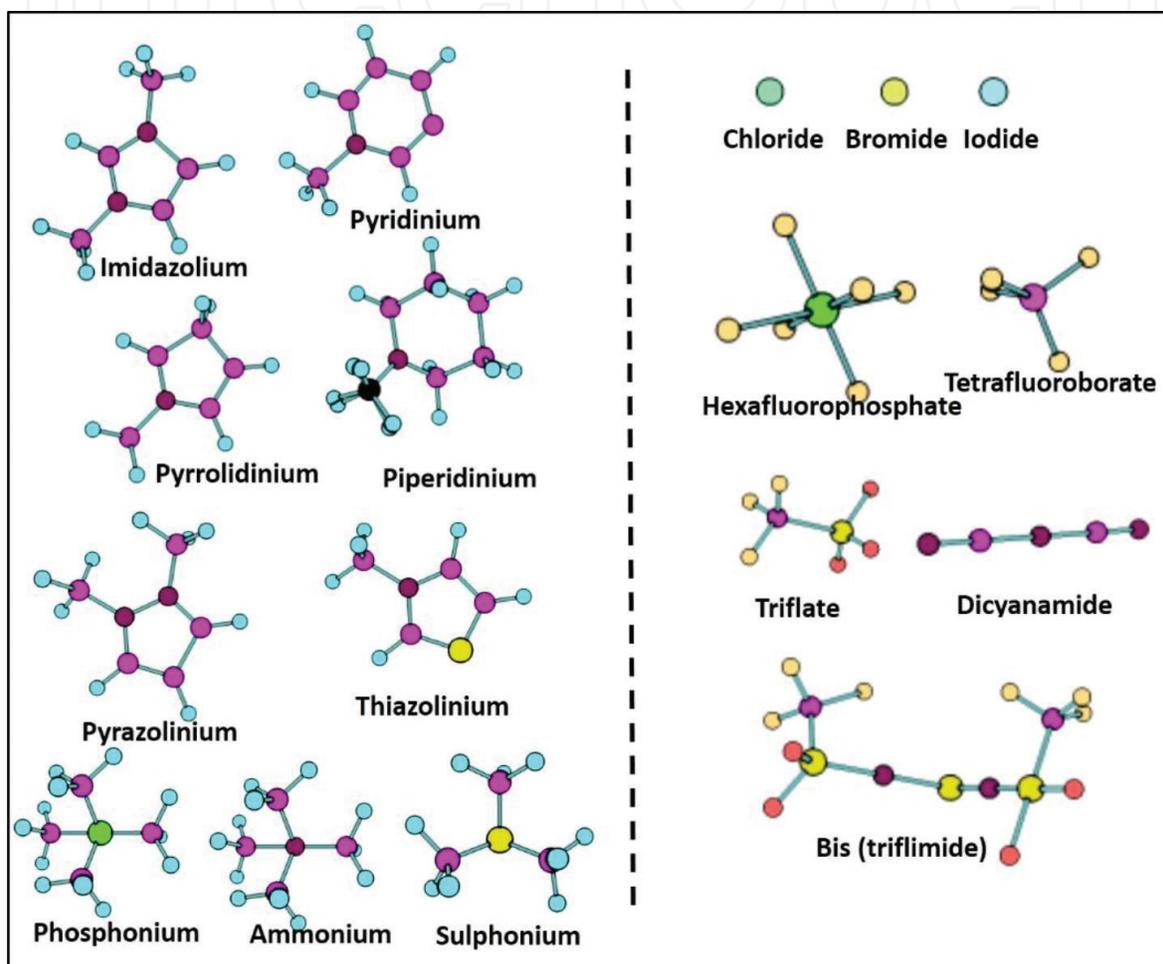


Figure 1. Common cations and anions of ionic liquids.

The structural design of ionic liquids is playing a very important role as it is decisive for controlling the temperature limits, self-assembly and associate functional properties. Self-assembly processes are mainly controlled by the type of cations, anions and side-chains. In ILs, only delocalised charge centres are present which makes the intra-molecular interactions less intense to gift them their exquisite properties. The organic cations and anions of ILs are often stabilised by resonance with highly delocalised charges. Ions with lower symmetry or without symmetry are another major feature of ILs, which restricts the molecular packing into a low-energy crystal structure, ultimately lowering the melting point [11, 12]. Their physical and functional properties could be well tuned, since they are capable for infinite number of

structural variation by changing cations, anions and the substituents [13–17]. They exhibit high degree of miscibility with a wide array of organic and inorganic materials, since they contain both organic cations and inorganic anions or vice versa. ILs is found to have higher affinity towards CO₂ and water vapour. This could be explored in devising gas separators for removing moisture or poisonous gases from the mixtures and also helping in CO₂ sequestration and reducing the greenhouse effect [18–22]. The main criteria for exploiting a compound as an electrolyte for electrochemical energy storage systems are high ionic conductivity, non-volatility, non-flammability, high thermal stability and good electrochemical window. Electrochemical window can be defined as the limiting potential range, in which, the electrolyte is electrochemically stable and is free from any unwanted redox reactions. As the electrochemical window of electrolyte is directly related to the energy density, high EC window is necessary for electrolytes for energy storage systems. In comparison with the commercially used electrolytes, ILs has greater ionic conductivities and better potential windows to draw superior energy storage performances. Unlike aqueous electrolytes with limited potential window less than 1 V, IL-based electrolytes have very high window of 3–4 V, very high ionic conductivity, very good liquidity range and thermal stability for efficient energy storage applications, such as electrochemical supercapacitors, Li-ion batteries, Na- or Mg-batteries, Fuel cells, etc. [23].

Compared to ILs, ionic liquid crystals (ILCs) are receiving importance in flexible electronics as safe and efficient electrolytes. They exhibit synergistic properties of both ionic liquids and liquid crystals. Just like ILs, ILCs are also solely composed of ions bound with ionic interactions in different extents. Liquid crystals are often regarded as the fourth state of matter, with ordering in-between highly rigid crystalline lattices and disordered liquid state. Mesophase formed between solid and liquid phases exhibit impressive properties due to positional order and flow properties. Rotating isotropic spherical molecules are responsible for the plastic crystal formation, whereas, the non-covalent interactions are behind the anisotropic behaviour of liquid crystals. Ionic interactions are often responsible for strong crystalline ordering, whereas, other non-covalent interactions like hydrogen bonding, van der Waals forces and layer-by-layer self-assembly are responsible for liquid crystalline mesophase formation. In addition to the cationic and anionic centres, long alkyl side-chains and functional groups are present in ILCs for modulating the mesophase self-assembly. They are the real smart materials for realising multi-functional applications, such as stimuli-responsive conductors for energy storage devices, electrochromic supercapacitors, flexible batteries, etc. Stimuli-responsive phase transition of ILCs enables to modulate the direction of ionic conduction in them as shown in **Figure 2**. Based on the order and texture of mesogens, mesophases exhibited by ILCs are mainly of two types: nematic phase and smectic phase [24]. Mesogenic molecules tend to align along the molecular axis in the nematic phase (1D ordered). Smectic phase is more ordered where the molecules are arranged in layers (2-dimensionally ordered). Based on the extent of ordering of mesogens within the layers, smectic phase is subdivided into Sm A, Sm B, Sm C, Sm D, Sm F, Sm G, etc. Sm A is the least ordered one, among all the smectic mesophases [25–28]. Tschierske defined the LC state as a condensed matter state, in which, there is orientational and/or positional long-range order in at least one direction and no fixed position for individual molecules [25]. Columnar and cubic phases are other major mesophases observed in ionic liquid crystals. Based on the lattice in which columns are arranged, columnar phase is divided into hexagonal columnar (Col_h), rectangular (Col_r) and oblique

columnar (Col_h) phases [29, 30]. Molecules with bent-core or banana shape displayed unique mesophases different from the normal mesophases [30–34].

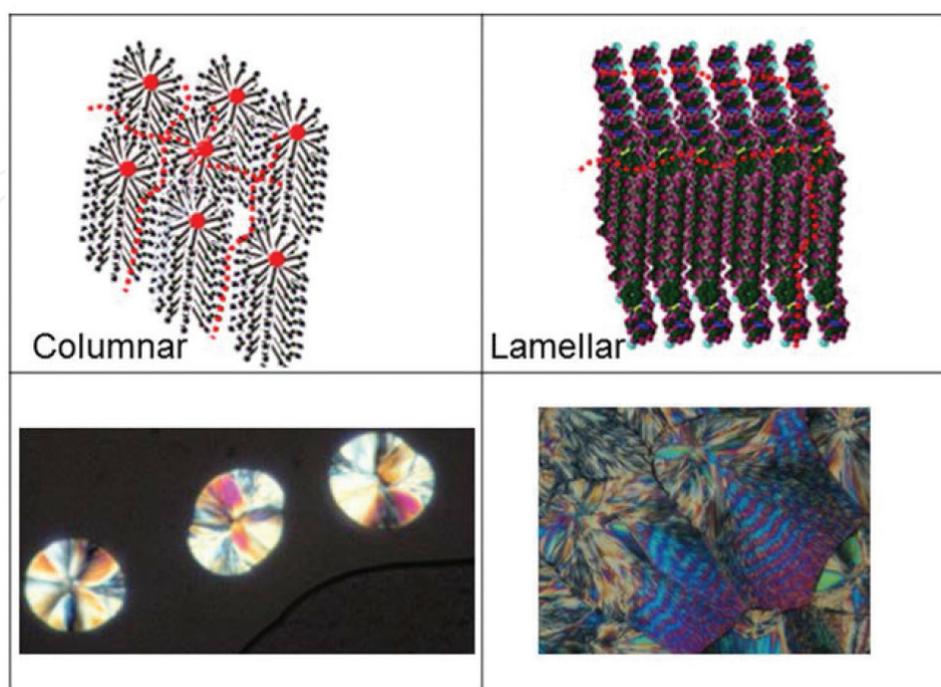


Figure 2. Conducting channels generated by the controlled self-assembly of ILCs. Columnar and lamellar phases with their polarised light microscopic (PLM) images.

Generally, for such mesophases, functional properties like refractive index, dielectric permittivity, magnetic susceptibility, conductivity, elasticity, etc. are measured to have different values in different directions (anisotropy). Since the molecular kinetic energy is high for the LC phase, it is capable to undergo self-adjustments in response to the external stimuli. For thermotropic ILCs, crystalline phase changes to mesophase on heating and then to isotropic phase on further heating. On cooling from isotropic melt, mesophase is revisited and finally crystalline phase on further cooling. If the mesophase is observed both in the heating as well as cooling ramp, such ILCs are known as enantiotropic ILCs. In some occasions, the mesophase is observed only during cooling from the isotropic phase. This type of ILCs belongs to the category of monotropic ILCs. Liquid-crystalline phase arises, due to the introduction of solvent or by varying concentration, which is regarded as lyotropic ILCs. On cooling the ionic liquid crystalline molecule from isotropic phase, the relative variation of intermolecular interactions and molecular kinetic energy leads to the formation of liquid crystalline mesophases. The alignment of charge carriers along the mesophase boundaries will produce conducting nano-channels for improving the ionic conduction [27, 28]. Mesophases exhibit characteristic birefringent textures, when examined under PLM.

LC phase in ILCs can be induced in response to thermal, concentration, potential, magnetic, light as well as mechanic stimuli. Unlike other stimuli, light could make the shift in conduction direction without making any physical contact with the mesophase, avoiding mechanical disintegration to the phase. Soberats et al. reported light-induced re-orientation of an imidazolium ionic liquid crystal effecting variation in the ionic conduction directions, transverse and longitudinal [35]. Mesophase formation of ILCs is accompanied with the formation of

nano-sized ionic channels in 1-, 2-, or 3-dimensions, due to the controlled self-assembly. These ionic channels are able to conduct charge carriers across the mesophase. The dimensions and directions of the nano-channels are controlled by the extent of self-assembly, and hence, the stimuli responsive mesophase formation can indirectly affect ionic conduction too [36, 37]. This photo-responsive ILC contains an azobenzene-core, which undergoes Cis-trans isomerisation when subjected to UV irradiation. Cis-trans isomerisation will shift the orientation of charge carriers, which are aligned in perpendicular direction to the molecular axis with concomitant mesophase transition from homogeneous to homeotropic smectic phases. Ordered charge carriers can be tuned and oriented with respect to external stimuli, which can be used as the electrolyte for various applications.

Liquid-crystalline phase formation of a quaternary ammonium ionic liquid crystal (QSs) in response to temperature or concentration by the controlled self-assembly of mesogens was studied from Sasi et al., recently [37]. Studies showed that the nature of the mesophase formed relies on the surface alignment of self-assemblies, topographical defects and molecular ordering, which are governed by various non-covalent interactions among the molecules, temperature and polarity of the solvent. Investigation of the LC phase formation, under PLM, reveals polymorphic textures including crystalline, plastic crystalline, nematic, hexagonal columnar phases, randomly oriented molecular layers as shown in **Figure 3**. In the nematic phase, molecular layers are uniaxially oriented and the plane of molecular layers may be perpendicular to the director. However, columnar layers are biaxially oriented and the molecular layers in this phase are perpendicular to the layer planes. A slight tilt in the director angle is responsible for the observation of various textures arising from the difference in the nature of defects.

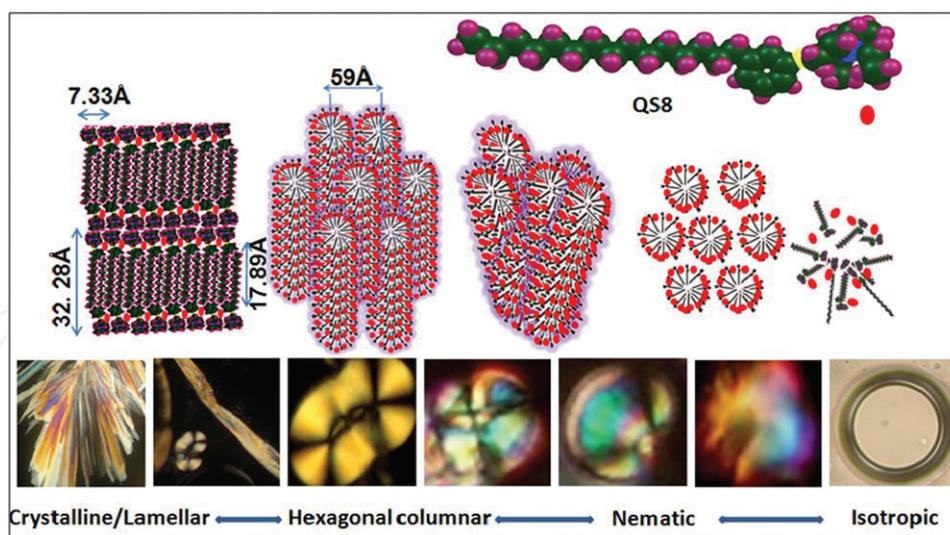


Figure 3. Mesophase formation by the self-assembly of mesogens and corresponding textural variation. Reproduced with permission from [37].

Generally, at room temperature, QSs are three -dimensionally ordered crystalline solids with highly birefringent spherulitic textures. During cooling from melt, they undergo transition to the gyroid-type of 1-dimensionally ordered nematic phase, further to hexagonal columnar phase by gaining the positional order. Further cooling may lead to the formation of lamellar and crystalline phases. Formations of conducting mesophase, in response to external stimuli, are mainly

attributed to the variation of molecular kinetic energy and the extent of intermolecular interactions. In the crystalline phase, molecules are tightly-packed together by means of very strong intermolecular interactions and consequently, they will exhibit the least amount of molecular kinetic energy. On the contrary, isotropic liquid is characterised by lower intermolecular interactions and very high molecular kinetic energy. Crystalline state has 3-dimensional orientational, positional and translational orders. But in the mesophase, the crystalline order is reduced and the degree of freedom of molecules gets enhanced so that a fluidic phase is resulted.

Ionic conductivity exhibited by ILCs is receiving significant importance and finding applications in electronic devices and drug delivery systems [38–46]. As the temperature increases, the 3-dimensionally ordered crystalline phase decreases and transforms into 2- or 1-dimensionally ordered LC phases, where there is more freedom for the transport of charge carriers, leading to higher conductivity. This conductivity enhancement with temperature is attributed to the thermotropic phase transitions that can be further envisaged from the temperature-dependent variation of charge diffusion coefficient (D) values. Similarly, lyotropic liquid-crystalline phase formation of the QSs is studied by means of conductivity and rheological analysis. Storage modulus increases with self-assembly and finally transformed into highly organized gel phase.

2. As electrolytes for energy storage systems

For any electrochemical energy storage systems (EESs), electrodes, electrolytes and separators are the main components [47, 48]. Electrolytes are considered as the heart of an EES, being the charge transport medium, which facilitates the ionic charge carriers for maintaining the device reactions alive. Electrolyte with good ionic conductivity and electrochemical window is necessary for exploiting maximum device performance [49]. Electrolyte plays an important role in controlling the cycle stability, rate capability, specific capacity and safety of the EESs. Choice of electrolyte is crucial in deriving the maximum output, since it could eliminate the possible parasitic side reactions effectively. Non-aqueous electrolytes have extended electrochemical windows to extract high energy and power densities. Conventional non-aqueous electrolytes used for energy systems are composed of ionic salts dissolved in volatile organic solvents. This is not at all safe, since there is a possibility of generating electric sparks when the system is charged at high rates, which can lead to the explosion of the device by burning easy flammable electrolytes. Also, the leakage of poisonous electrolytes while crimping the cell or on standing for long will also create serious environmental problems. ILs and ILCs with high ionic conductivity, high EC window and environmentally benign nature prove to be better alternates for conventional electrolytes in realising high performing energy storage devices [50]. Solid electrolytes like gel-polymer electrolytes and ionogels electrolytes, which are derived from ILs, are also found to be suitable for powering energy storage systems. Ion-conducting polymeric films can also be prepared by cross-linking the polymerizable side-chains in the self-assembled systems including liquid electrolytes, plasticisers and polymerizable mesogens. Also, ILCs with ordered ion channels were found to be extremely advantageous over conventional I^-/I_3^- couple, which shuttles the energy transport in dye-sensitized solar cells (DSSCs). This book chapter reviews various ILs, ILCs and their derived electrolyte systems employed for various energy storage systems and their advantages over conventional electrolytes.

2.1. Supercapacitors

Supercapacitors are widely employed as electrochemical energy storage devices as a replacement or complementary to batteries. High power density, faster charge-discharge rates, better cycle stability and service life of supercapacitors make them far superior to other energy storage systems [51]. They found to be more common in industrial and automobile applications rather than consumer electronics. Unlike batteries, which need considerable time for initial recharge, supercapacitors possess faster charge and discharge to facilitate regenerative pulse and peak assists necessary for starting the engine. Their capacity to generate intense high power discharge in short periods could be suitable to produce flash lamps for aerospace applications. Faster responses of supercapacitors are attributed to fast surface processes like adsorption or desorption of charge carriers at the electrode-electrolyte interface.

Based on the charging mechanism, supercapacitors are divided into two categories, such as electrical double-layer capacitors (EDLC) and pseudo-capacitors. In EDLC, the electrical energy is stored by the formation of Helmholtz double layers at the electrode-electrolyte interface. The width of the charge separation influenced the capacitance of the device to a great extent. In EDLC, the storage mechanism mainly involves the adsorption and desorption of charge carriers on the porous organic electrodes. Various porous carbon derivatives, such as graphite, mesoporous activated carbon, CNTs and conducting polymers were frequently employed for performing the function of porous electrodes. Capacitive action of pseudo-capacitors involves the charge transfer in-between the electrodes by means of faradaic reactions. Normally transition metal oxide derived electrodes which can provide smooth electron transfer were deployed for generating high-performing pseudo-capacitors. Symmetric and asymmetric supercapacitors are differed by the nature of electrodes used for fabricating them. Two electrodes with identical capacitances are used for fabricating symmetric supercapacitors, but two distinctly different electrodes are used for asymmetric supercapacitors [52].

Device structure of supercapacitors constituted by two same or different electrodes, are separated by an ion-transparent dielectric membrane wetted with ionic electrolytes. On charging, the electrodes get polarised, so that, the ions from the electrolyte will migrate towards oppositely charged electrodes and gets adsorbed over the electrode surface resulting in the formation of double layers. Each electrode will associate with a layer of diffused charges from the electrolyte, and hence, the whole device will function as two capacitors separated by a resistor. Double-layer capacitance (C) is directly related to the specific surface area (S) of the electrodes and inversely related to the distance (d) between ions and electrodes.

$$C = \frac{\epsilon_0 \epsilon_r S}{d} \quad (1)$$

So, activated carbon electrodes with very high surface area are tenable to deliver extremely high capacitive behaviour. If C₁ and C₂ are the individual capacitances, then the total capacitance of the entire device can be given as,

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} \quad (2)$$

The storable energy of a capacitor quadratically related to the potential window of the electrolyte is ,

$$E = \frac{1}{2} C V^2 = \frac{1}{2} QV \quad (3)$$

where, V is the potential window and Q is the charge stored in the capacitor. The potential window is limited by the decomposition potential of the electrolyte used. In the case of aqueous electrolytes, it is not possible to go beyond 1 V, whereas for non-aqueous electrolytes, the decomposition potential is quite high to deliver very good energy density. Acetonitrile-based systems could be used up to 2.8 V and propylene carbonate-based systems can go around 3 V. Potential-driven break down of dielectric material will also affect device performance, which will limit application of very high potentials also. As pointed out earlier, de-merits of conventional electrolytes pave the way for new non-conventional safety electrolytes for powering supercapacitors [53]. Initially, ILs was used as high-conducting electrolytes for supercapacitors by dissolving in suitable solvents. Even though they have extra-high conductivity and performed exceedingly well with porous carbon electrodes, the energy density is limited by the decomposition potential of the solvent used. ILs with excellent electrochemical window, generally greater than 3 V, could be used alone as high-conducting electrolytes. Anions of ILs are oxidised only at high potentials and the reduction of cations also require very low potentials, giving them very high electrochemical windows and rendering very high energy densities. In comparison with ILs with halide anions, the ones with fluorine containing coordinate anions displayed higher EC windows. Apart from the EC window, ion size, ion type, interaction of ions with solvent and electrodes will also influence the overall performance of the devices [54]. Equivalent series resistance (ESR), an important quality parameter of supercapacitors, is strongly influenced by the ion type, conductivity as well as the viscosity of the electrolyte. If the ions are too heavy, less diffusible or too viscous, it will considerably drag down the electrolyte conductivity and increase the ESR. This will affect the storage efficiency, as the ESR is inversely related to the power density of the device as,

$$P = \frac{V^2}{4 \cdot ESR \cdot m} \quad (4)$$

where V represents the potential window and m is the active mass of the electrodes. Also, the interaction of the electrolytes with solvents or electrodes also has a strong role to play in deciphering the cycle stability of the system. High temperature stability of ILs was found to be promising in exploiting them as electrolytes for powering supercapacitors for a wide range of temperatures. Delivering power at extreme condition seems to be difficult with conventional electrolytes, as they may be either in frozen or gaseous state in which the charge conduction is impossible. Inception of ILs with wide liquid range helped to solve this difficulty to a greater extent. This will be suitable in producing high-power short-pulse arc lamps for polar regions, space stations and in mines. It was found that the viscosity of ILs could be reduced by suitable formulation of eutectic mixture of two or more ILs with identical anions, which can also be applied to a wide range of temperatures due to the depression in freezing points of ILs.

Lin et al. reported the use of a mixture of piperidinium and pyrrolinium ILs for preparing the electrolyte for supercapacitors for temperatures ranging from -50 to 100°C [55]. It delivered an outstanding capacitance of 180 F/g , which was attributed to a wide EC window of 3.5 V . Similarly, Ruiz et al. demonstrated a mixture of pyrrolidinium IL in butyronitrile as power electrolyte for supercapacitors for temperatures ranging from -20 to 80°C [56]. Low-viscous ILs has higher conductivity and capacitive performance than high-viscous ILs, due to better ionic mobility. Likewise, variation of anionic or cationic sizes also has a prominent effect on the performance. ILs with PF_6^- or BF_4^- anions have better capacitive performance over other anions, because their ionic size is complementary to the pores of the mesoporous carbon electrodes, which is widely employed in supercapacitors. Clever structural design of ILs could also improve the device performance. Rennie et al. extensively studied on this aspect and found that the ILs with ether-bonded alkyl side-chains possesses higher capacitance in comparison with others. They found that the presence of ether bond could induce significant flexibility to the structural design. It could lower the viscosity and further enhance the conductivity, which in turn improves the capacitive performance [57]. Xu et al. explored a new kind of ILs with fluorohydrogenate anions with comparatively lower viscosity and better ionic conductivities to be used as conducting medium in a wide range of applications, mainly supercapacitors and other energy storage systems [58].

Like ILs, their solid analogues and secondary derivatives, such as ILCs, ionogels, etc. are also receiving technological importance in energy storage systems [59]. Presence of well-ordered conducting channels provide them strong propensity to transport and store charges. ILCs could be explored as electrolytes either in the solution state in suitable solvents or in their conducting liquid crystalline mesophase. Thermotropic mesophase formation improves the molecular conductivity to extract better capacitance at high temperatures. We have exploited the lyotropic mesophase formation of an imidazolium ionic liquid crystal in acetonitrile to derive a high-conducting electrolyte for supercapacitors. Unlike pure solution, where the ion density is very low, liquid-crystalline phase have high ionic density and weight-specific performance to yield superior performance. Not only the ionic concentration, but also the ionic mobility is important in governing the storage performance. Lyotropic columnar phase of ILC found to be adequate with conductivity and lower viscosity to be employed in supercapacitors as electrolytes. In mesophase, self-assembly of mesogens provide adequate nano-oriented pathways to effect charge diffusion with ease for developing double layers in response to the subjected potential. Lyotropic columnar mesophase yielded a specific capacitance of 134 F/g with 80% capacitance retention, after 2000 cycles [60]. Schematic diagram showing the capacitive behaviour of ionic liquid crystalline electrolyte in powering high-performance supercapacitors and corresponding liquid crystalline phases are given in **Figure 4**.

In the LC phase, the charge carriers are aligned by the molecular self-assembly and have considerable degree of freedom to migrate to corresponding electrodes on charging, forming electrical double layers. While on discharge, when the electrodes are depolarised, ions move away from the electrodes to the centre depleting the double layers. These processes are highly reversible to achieve better cycle stability. Solid ionic electrolytes have also been obtained by mixing ionic liquids with polymer binders or carbon materials to generate safe energy storage systems. Zhang et al. prepared a flexible gel-polymer electrolyte containing

1-butyl-3-methylimidazolium chloride and Li_2SO_4 in a matrix of poly(vinyl alcohol) to be used as flexible safe electrolyte for supercapacitors [61]. The high ionic conductivity and a high fracture strain of the electrolyte is benefited by delivering a specific capacitance of 136 F/g, with a maximum energy density of 10.6 Wh/kg and a power density of 3400 W/kg. The conductivity and capacitive behaviour of supercapacitors remains with negligible fade, even after the repeated bending cycles illustrated the flexibility of electrolyte and its application in future plastic electronics. Similarly, many reports are there in utilising ILs or ILCs in combinations with PEO, PVDF, PHEMA, etc. to materialise highly conducting and flexible ionogels for powering supercapacitors.

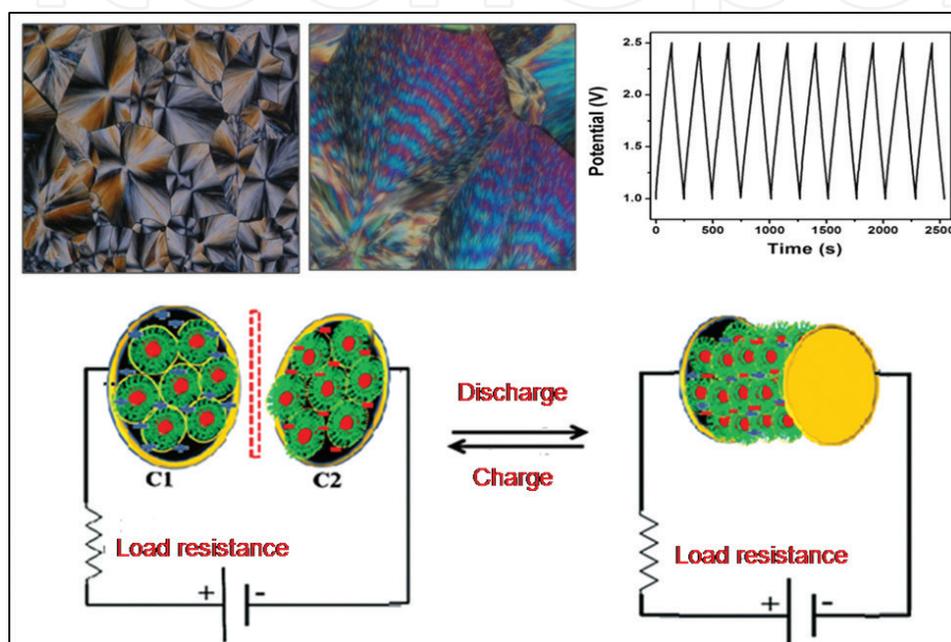


Figure 4. Bio-based ionic liquid crystal as electrolyte for supercapacitors. Reproduced with permission from [60].

2.2. Lithium-ion batteries

Like supercapacitors, or comparatively to a higher extent, Li-ion batteries attracted the scientific interest particularly because of its higher energy density and superior performance [62, 63]. In Li-ion batteries, device structure is more or less similar to that of supercapacitors with a separator soaked with electrolyte, sandwiched in-between a pair of electrodes (cathode and anode). A typical device structure of the Li-ion battery is depicted in Figure 5. Similar to pseudo-capacitors, the energy storage is realised by the Li-ion transport across the permeable separator. Leakage and flammability issues associated with conventional volatile organic electrolytes lead to the inception of safe, cost-effective and eco-friendly electrolytes, mainly ILs [64]. Low evaporation power and less flammable nature make them more safe and convenient. Initially, quaternary ammonium or phosphonium salts with triflate anions were explored for electrolyte applications. Less viscous and cathodically stable ILs are necessary for effective lithium cycling. Fluorinated anions, such as BF_4^- , PF_6^- , TFSI⁻, etc. were found to be more efficient in realising better Li intercalation reactions. As the size of anion significantly affects the ionic transport, Matsumoto et al showed high-rate cycling of Li/LiCoO₂ cell with smaller sulphonamide anions [65].

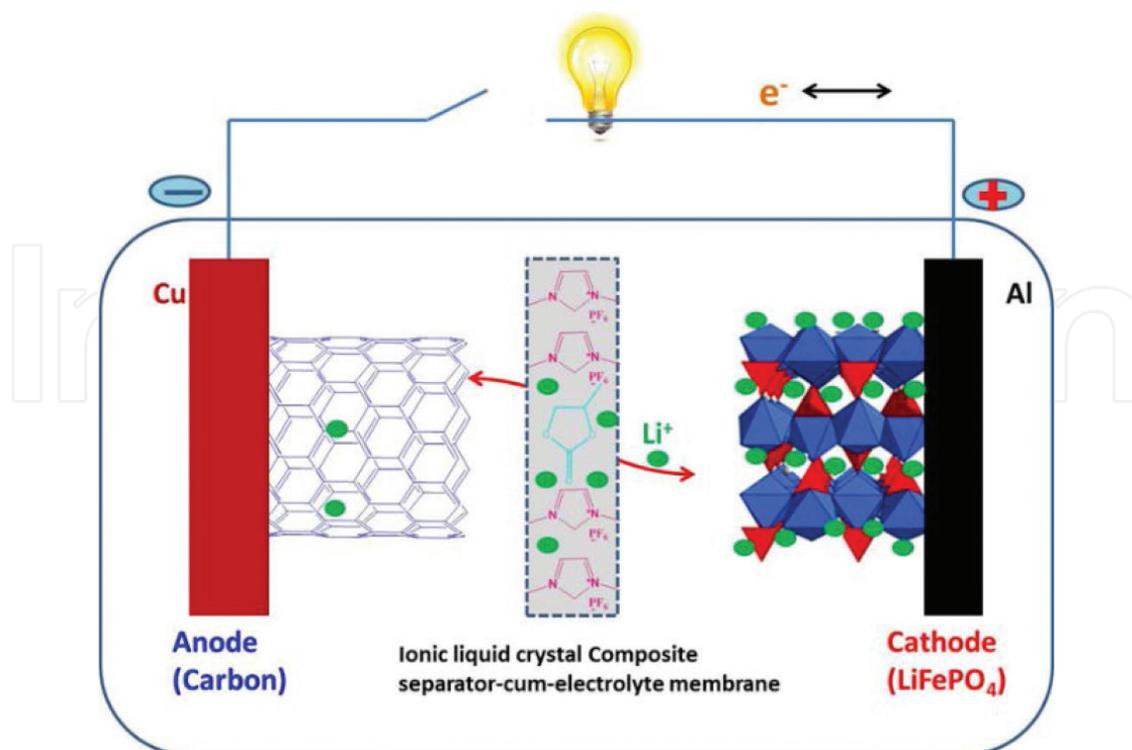


Figure 5. Design of Li-ion battery incorporating ionic liquid crystal membrane separator.

It was observed that bulkier cations of ILs, sometimes, form inhibiting layers on the surface of carbonaceous anodes hindering cell reactions. Fluorinated anions are able to remove such unwanted layer formation and rule out the need for secondary additives for this purpose. IL-based electrolytes demonstrated their excellent performance with variety of electrode materials. High redox stability of ILs will help to explore new horizon of electrodes with high-voltage stabilities, so that the energy and power densities could be improved [66]. The main factor, which needs to be addressed while choosing a solvent for Li batteries, is the handling of dissolved Li-ions and its influence on charge transport, while cell reactions are on. Structural design of ILs by incorporating anionic or cationic functionality to interact with dissolved ions or the usage of external additives or diluents were also tried to eliminate filament formation and other undesirable reactions by the dissolved Li-ions. IL structural design has a special role to play on the formation of protective film (solid electrolyte interface, SEI) and also to modulate ion transport, charge transfer and electrolyte stability [67]. Each ILs has definite reaction pathways for modulating the Li-ion transfer, depending on the association or other interaction of the constituting ions. Considering the needs, such as safety, sustainability, strength, cycle stability and high temperature operability, new designs and methodologies were introduced. Inception of thin and flexible batteries further added much interest towards IL-based electrolytes. Even though many studies have invested to analyse the energy storage performance of IL-based electrolyte in combination with a large array of electrode materials, the commercialisation of them is still uncertain. High-cost of ILs, in comparison with conventional carbonate solvents, may be one of the major hindering factors. In order to solve the situation, efforts were taken to reduce the cost of ILs by introducing new low-cost cations or anions with simple

strategies. Bio-based ILs/ILCs with negligible production cost and comparable performance could be prepared by suitable modification of industrial waste by-products like cashew nut shell liquid (CNSL). They can be used for powering energy storage systems either as such or in combination with solvents or as solid films or gels with suitable polymeric binder. Since the conversion of waste to value-added electrolytes seems to be a double benefit to the society, it can be a remedy for pollution as well as a sustainable energy storage pathway. Similarly, dicyanamide $[N(CN)_2]^-$ with highly delocalised negative charge proves to be a better alternate for fluorinated anions to produce low-cost ionic liquids. Their highly delocalised ionic charge is responsible for the extremely low freezing points, which they have [68].

Thermo-mechanical stability of ILs/ILCs is utilised for generating stable batteries with different categories of electrodes and with good cycling stability. Rate performance of the cells also found to be improved, due to the better conductivity, tuneable viscosity and reversibility of IL-based electrolytes. But, in some cases, rate capability is significantly affected by the ion-association with ILs during cell cycling, which enhances the viscosity and thereby hinders cycling efficiency. In contrary to this, fluorosulfonamide anion containing ILs displayed high-rate performance with higher Li-ion concentrations, but lacked the device stability. Mixture electrolytes containing ILs and conventional solvents, found a better strategy to cope up with the desired conductivity and device stability. Recently, newer electrode combinations such as Li-air, Li-S, Na, Mg and Al batteries have formulated to overcome the shortcomings of Li-ion batteries [69]. In all these new-generation batteries also, ILs seems to be a better alternate for ionic shuttling. Their wide operation window and liquid range will be applicable in many more upcoming storage systems.

Solid-state electrolytes, which could function as both electrolyte and separator, could be generated by integrating ILs/ILCs with polymeric binders [69]. Schematic diagram showing the separator composed of ILC-based hybrid membrane that functions as both separator and electrolyte is given in **Figure 5**. High conductivity, porosity, better Li-ion transport, high electrolyte affinity and uptake, mechanical stability and thermal stability are the main requisites for solid electrolytes [70]. Kato et al. developed thermotropic liquid crystalline (LC) electrolytes for lithium-ion batteries for the first time by the self-assembly of rod-like LC molecule having a cyclic carbonate moiety with lithium salts and is used to form self-assembled two-dimensional ion-conductive pathways. Electrochemical and thermal stability and efficient ionic conduction is observed for the liquid crystal and is employed as an electrolyte in lithium-ion batteries with highly reversible charge–discharge for both positive and negative electrodes [71]. Presence of ambiphilic ILs/ILCs will definitely improve the electrolyte affinity and further ionic transport upheld the reaction kinetics and improves efficiency. Flexible, wearable storage batteries are the future directives of new age storage systems.

2.3. Fuel cells

Fuel cells are unanimously agreed to be one of the green technologies for sustainable energy, due to their high energetic efficiency and low environmental impact. These devices directly convert chemical energy to electrical energy with water as by-product, thereby omitting toxic emissions prevalent with fossil fuels [72]. They have been explored in space crafts and subma-

lines to power the arc lamps and to make use of by-product water for drinking purpose. The major working elements of fuel cells are bipolar plates, diffusion layers, electrodes (anodes and cathodes) and the electrolytes. Mainly, aqueous solutions with acidic or basic nature have been used as the electrolyte for conventional fuel cells. Even though fuel cell technology possesses an eventful 150-year-old history, no one had succeeded in using proton carriers other than hydronium ions or hydroxide ions in a fuel cell, until last few decades. Obviously, it confined the fuel cell science within the aqueous electrolytes of acid or basic character. The effective potential range also limited below 1 V, due to the use of aqueous electrolyte alone. In addition, the operating temperature range also limited to below 100°C, when aqueous electrolytes are employed. In proton exchange membrane (PEM) fuel cell, the core is called the membrane electrode assembly (MEA), which comprises the PEM placed between two electrodes. Different functions of PEMs are separating the gaseous reactants, conducting protons from the anode to the cathode, electrically insulating the electrons and supporting the catalyst. The necessary requirements an exchange membrane should have to function exquisitely are excellent proton conductivity in dry and wet states, unflinching mechanical strength and dimensional stability, chemical, electrochemical and thermal stability under the working conditions, low fuel and oxygen crossover, easy conformation to form a membrane electrode assembly and low-cost **Figure 6** [74, 75].



Figure 6. Application of protic ILs in fuel cells as electrolytes. Reproduced with permission from [73].

Nafion (perfluorosulfonic acid) ionomer is one of the most widely used membranes in PEMFC devices because of its chemical inertness, high ionic conductivity and better mechanical strength. But, the conductivity of the Nafion usually reduces when the temperature goes beyond 100°C, as the evaporation of water will hinder the ionic mobility considerably. Even then, elevated temperatures are advantageous because the contamination tolerance of the catalyst is improved and even low purity hydrogen could be benefited at higher temperatures. It would also eradicate both carbon monoxide poisoning and noble metal catalyst corrosion frequently associated with aqueous electrolytes. In addition, electrode reaction kinetics also improved at elevated temperatures. All these issues could be solved by introducing room temperature ionic liquids as the electrolytes either by gelling ILs with polymers or polymerizing polymerizable ionic liquids. Protic ionic liquids could be generally considered as a salt of a Bronsted acid and a Bronsted base. The transfer of a proton from an acid to a base

leads to the formation of hydrogen-bonded networks between proton donor and acceptors. Protic ILs with more fluidity found to have more conductivity also underlines that the conduction follows vehicular mechanism. IL-based solid electrolyte membranes have exquisite conductivity and thermo-mechanical stability and are also free from water. Mainly, azoles like imidazole, pyrazole, triazole, benzimidazole, etc. or amines are the proton relay molecules in IL-based electrolytes with a wide pH range, which opens a new horizon to design alternate low-cost electrode materials, with an aim to replace expensive and scarce platinum electrodes. Protonated imidazole derivatives are found to have an excellent conductivity and it conducts like water through Grotthuss conduction mechanism [76–78].

The main challenge in employing ILs in PEMs is choosing the suitable molecular design of the ion pair, so that the whole requirements for the membrane electrolyte in a fuel cell including mechanical stability without compromising the proton transport activity are attained. Lee et al. fabricated a SPI/[dema][TfO] membrane for PEMFCs under non-humidified conditions, which fetch a peak power density of 100 mW cm^{-2} and maximum current density of 400 mA cm^{-2} at 120°C [73]. However, this membrane has an unstable three-phase boundary in the catalyst layer formed by leaked [dema][TfO]. Lee et al. reported many fuel cell varieties with the ILs provided by Ohno et al. [79]. But, the mechanical integrity of the solid electrolytes needs to be improved. Relatively, a new approach for fabricating mechanically stable and high-conducting solid electrolytes is the polymerization of ionic liquid monomers. Ionic liquid monomer $[\text{HSO}_3^-\text{BVI}][\text{TfO}]$ was polymerized by Díaz et al. and employed in a PEMFC at 25°C under anhydrous conditions, measuring a maximum current density of 154 mA cm^{-2} and a peak power density of 33.1 mW cm^{-2} [80]. These membranes were thermally stable up to 300°C . Utilisation of organic plastic crystals or ionic liquid crystals as high-conducting solid safety electrolytes is another intriguing strategy. Membranes based on the cellulose acetate supported with [choline][DHP] doped with various acids were studied by Rana et al. [81]. Belieres et al. recently identified that the small cation NH_4^+ could be useful in replacement of H_3O^+ [82]. Also, IL-based electrolytes with nitrate anion prove to have narrow ranges of current density, in which, there appears to be almost no energy barrier to oxygen reduction. The reasons for this are still not clarified, though they are presumably related to some instability of the nitrate anion. Hagiwara et al. proposed the application of fluorohydrogenate ionic liquid in fuel cells [83, 84]. In principle, the FHFC needs no humidification, since the fluorohydrogenate ion conduction does not require the presence of water. They have also demonstrated composite membranes consisting of 2-hydroxyethyl methacrylate (HEMA) and EMPyr(FH)1.7F and achieved a maximum power density of 200 mW cm^{-2} .

2.4. Dye-sensitized solar cells (DSSCs)

DSSC is a third-generation photovoltaic device, which can convert solar energy into electrical energy in a more convenient and cost-effective way than the conventional semi-conducting photovoltaics [85]. They can be also designed as flexible and multi-coloured forms. The device structure of DSSCs include a photosensitizer (often organic dyes that is why the name dye-sensitized), a photo anode comprised of semiconducting nano-particles with well-adjusted conduction band to accept electrons, a counter electrode (mainly Pt based) and electrolyte. The theoretical maximum efficiency that could be extracted from a DSSC is around 20% only,

but simple and convenient device structure, easy fabrication and comparatively low cost active materials made DSSC so popular. As we pointed out electrolyte is one of the major components of DSSC, the main function of which is to facilitate a conducting pathway to keep the electron transfer mechanism alive by regenerating the oxidised dye by providing electrons.

Normally I/I_3^- couple in acetonitrile is used as electrolyte in DSSCs to regenerate the dyes. Volatile solvent and toxic additives make the use of this electrolyte undesirable even if they gave very good efficiency. Repeated exposure to the solar heating may evaporate the solvents so that the device efficiency lowered due to poor charge transport. Quest for alternate electrolytes found ILs/ILCs as one among possible candidates. Combination of redox active salts with ILs is often employed for generating the ionic couple which can produce faster charge transport. Viscosity and conductivity of ILs are the determining factors for improving charge transport. High-viscous ILs often fails to harvest good efficiencies owing to poor ionic diffusion and transport. Eutectic mixtures of ILs were employed by many groups as a low-viscous high-conducting electrolyte system with good efficiencies. It was also found that addition of Lithium salt with IL in combination with TiO_2 based photoanode could lower the conduction band of TiO_2 to improve the electron injection between dye and TiO_2 [86]. Similarly more basic anions like dicyanamide will also influence the conduction levels to modify the V_{oc} of DSSC and thereby efficiency. Better redox couple diffusion, fast electron transfer, slow recombination due to high electron diffusion lengths, excellent electrochemical reversibility are the main advantages of using IL based electrolytes over conventional ones. Even then, the paradigm remains in finding appropriate ILs with energy levels closer to the dye for its fast regeneration, but at the same time it should be in a level so that V_{oc} remain unaltered. Cobalt based redox couples have used very recently in harnessing very high efficiencies; a positive sign. Cobalt based systems in conjugation with ILs may lead to much better performances. Since the efficiency of DSSC is influenced by a large number of factors optimisation of each one with IL electrolytes is essential. Different photosensitizers like porphyrins, Ru-based inorganic dyes, organic molecules, etc. have been studied for solar energy conversion in combination with IL electrolytes. A porphyrin based dye recorded a 4.9% efficiency with $[C_2mim][B(CN)_4]$ -based IL electrolytes [87–90].

ILs and ILCs are more suitable for flexible DSSCs since they could be easily formed in the form of thin films with the combination of some polymeric binders. Large scale batch to batch production of thin film electrolytes will definitely revise the face of modern solar technology. Easy miscibility of ILs with conventional polymers and non-volatility made them highly desirable for safe, flexible and durable energy conversions. Moisture sensitivity and atmospheric stability of the electrolyte membranes should also be optimum. Instead of easy corrodible ITO/FTO electrodes new stable substrates have to be designed and developed for working with IL based electrolytes. Semiconducting metal nano-particles, carbon derivatives and polymers can also function as electrode materials.

Quasi-solidified electrolytes obtained by gelling ILs with polymers or ionogels can also utilised for DSSCs. It will reduce leakage problems, improve connectivity, flexibility, etc. Use of ILCs as electrolytes is another possible option. Being solid-state analogues of ILs,

ILCs have ions with a definite structural order to impart excellent solid-state conductivities. They could be further exploited for stimuli responsive conduction or temperature dependent storage, etc. Modern device structures for performing under dim light or extreme conditions will be in reality when combined IL/ILC electrolytes. It will also be suitable for wearable or stretchable device architectures to harness energy in a more sustainable manner.

Quasi-solid electrolytes were also developed by dissolving poly (ionic liquid) in room temperature IL harvested a good PCE of 5.92% with excellent long-term stability. The superior performance is attributed to the improved conductivity owing to the extended charge transport networks via the π - π stacking of imidazolium rings [91]. Gunko et.al prepared new electrolytes by suspending smaller amounts of graphene flakes in RTILs to extract more than 25 times improved photovoltaic performance [92]. Kuang et al. used carbon black- IL mixture as better performing electrolyte without adding iodine to yield 6.37% [93]. Jang et al. used an efficient ionic plastic crystal derived from imidazolium iodide salt as an excellent electrolyte for solid-state DSSCs with high PCE of 7.8% [94].

The plastic crystal electrolyte membrane was fabricated over the dye-adsorbed TiO_2 by melt processing. Wang et al. developed ionogels with silica nano-particles and ILs is to used as high-performing solid DSSC electrolytes [95]. Schematic diagram showing the electronic transfer between silica-ionic liquid quasi-solid electrolytes to the dye to re-generate it on photo-oxidation in solid-state DSSC is given in **Figure 7**. Polymer electrolytes composed of conventional polymer binders and ionic liquids could also employed for solid-state DSSC applications. Recently, Kato and co-workers developed high-temperature stable liquid crystalline electrolytes for DSSCs. The self-assembly of a carbonate mesogen and an IL forms 2D ion channels for the smooth passage of I^-/I_3^- couple, harvesting till date better performance up to 120°C . Utilisation of ionic liquid crystalline electrolytes helps in fabricating quasi-solid-state DSSCs with excellent power conversion efficiencies over a wide temperature range.

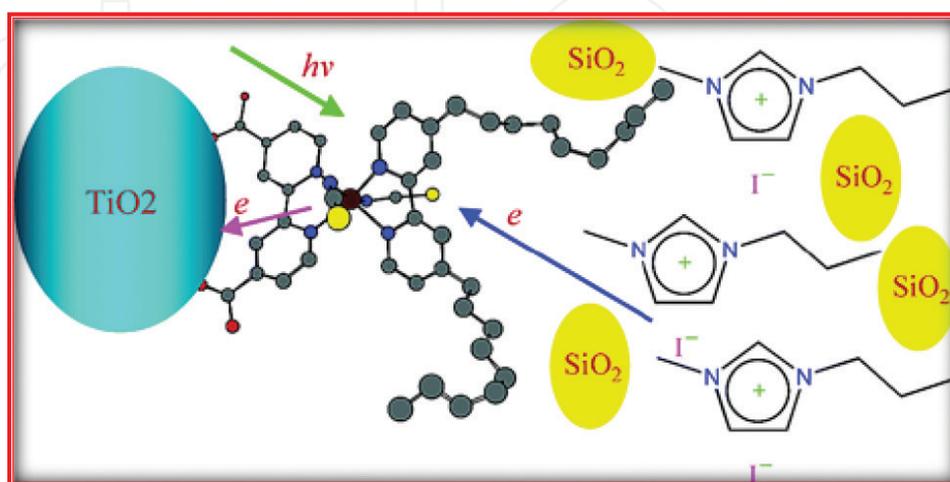


Figure 7. Quasi-solid-state electrolytes based on ionic liquids for DSSCs. Reproduced with permission from [95].

2.5. Other applications

Apart from the above discussed energy applications, ionic liquids and ionic liquid crystals were also exploited in systems like thin film transistors, thermo-electrochemical cells, hydrogen storage applications, etc. Application of ILs/ILCs with more eco-friendly nature will generate safe and sustainable energy storage for the future. Application of ILs as gate electrolytes in thin film transistors has paved way to the modern flexible electronics [96–99].

3. Conclusions

The present survey on the electrolyte systems used in various energy devices suggests that ionic liquid crystals are demonstrated as efficient electrolyte systems because of their anisotropic phase induced exciting channels, such as high ionic conductivity and diffusion along with excellent thermal stability, low dimensionally ordered phase, low vapour pressure and non-toxicity. They can be considered as prospectable and sustainable materials for bringing safe and affordable electronic devices. Their ability to formulate solid electrolyte films, in combination with polymers, can make revolution in the field of flexible, wearable, bendable supercapacitors, fuel cells and batteries.

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