

Received:
29 May 2018

Revised:
10 September 2018

Accepted:
4 October 2018

Cite as: Rafida Sahrash,
Asima Siddiqua,
Humaira Razzaq, Tahir Iqbal,
Sara Qaisar. PVDF based
ionogels: applications towards
electrochemical devices and
membrane separation
processes.
Heliyon 4 (2018) e00847.
doi: [10.1016/j.heliyon.2018.
e00847](https://doi.org/10.1016/j.heliyon.2018.e00847)

Review Article

PVDF based ionogels: applications towards electrochemical devices and membrane separation processes



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Abstract

Ionogels have emerged as one of the most interesting and captivating form of composites which credits to the outstanding characteristics. One of the most important constituent of ionogels is ionic liquid, which show many attractive properties notably non-volatility, in-flammability, negligible vapor pressure, tunability, thermal stability and solvating ability. A large variety of matrix materials have been under consideration for ionogels, presently, polymer/ionic liquid based ionogels have attracted much attention. Numerous polymeric materials such as have been utilized for these polymer/ionic liquids based ionogels. Polyvinylidene fluoride (PVDF) has been on top of the line as a matrix material for polymer based ionogels owing to its stability, aging and chemical resistance and mechanical strength. This review is primarily concerned with the properties of polyvinylidene fluoride based ionogels with an emphasis on their applications in various domains electrochemical devices, gas separation and liquid/liquid separations.

Keywords: Materials chemistry, Materials science

1. Introduction

A gel is defined as “a solid interconnected network spreading throughout the liquid phase”. An ionogel is therefore a kind of gel that essentially contains an ionic liquid in it. In gel, the solid acts as a continuous phase whereas the liquid acts as a dispersed phase. It is a cross-linked three dimensional network which is mostly amorphous hydrous oxide [1]. Ionogels serve as a highly significant class of composite materials which unifies the properties of both solid and liquid components keeping the main properties of IL [2]. Mostly the matrix concentration in ionogels can be very little such as in case of silica matrix, it varies from 2-3%. Ionogels differ in chemical composition from fairly rigid solid to soft material depending upon the chemistry of ionic liquid and other factors [2, 3]. Ionic liquids can be more advantageous when they are immobilized solid supports, this reduces issue of leakage of ionic liquid from matrix. Ionogels exhibit remarkable mechanical [3], conductive [4], thermal [5] and rheological properties [6] in addition to certain other properties that makes them a widely investigated class of composites.

There are two fundamental classes of ionogels which include physical gels and chemical gels. Physical gels usually exist in the form of jellies, pastes or slurries and are formed because of physical or non-covalent interactions like hydrogen bonding etc. Chemical gels, on the contrary, are formed as a result of covalent interactions and have an inorganic matrix material [7].

Recently, ionogels materials having polymer matrix have emerged as a new class of ionogels. The growing interest in the field of these polymeric ionogels is mainly motivated by ionic liquids which act as a fundamental component of these ionogels [8]. The polymer/ionic liquid based ionogels essentially consist of polymer matrix material as a continuous phase and ionic liquid as a dispersed phase [8]. Hence these polymer based ionogels have been essentially defined as a polymer network formed with in an ionic liquid phase [9]. The polymer/ionic liquid based ionogels have established their worth in many areas of life notably actuators [10], sensors [11, 12], fuel cells [13] and dye sensitized solar cells [14]. The increasing number of applications of polymer/ionic liquid based ionogels is mainly attributed to the lightness, flexibility, durability, resistance to undesired atmospheric effects of polymers in addition to their ability of forming networks with large number of organic and inorganic materials [15]. The mechanical properties of ionogel in all-solid state energy device are very good point which is very important but rarely reviewed in other papers. Ionogels have the great potential to be used in all-solid-state/flexible/wearable energy devices. Some mechanical strength tests such as rheology, compressive, stretchable performances have been studied by researchers [16, 17]. One very

important advantage for ionogel is their high thermal and electrochemical stability with wide temperature range for high/low temperature electric devices applications [17]. Moreover, the remarkable properties of ionic liquids incorporated in the polymer matrix material also make polymer/ionic liquid based ionogels, an important class of ionogels. There occur numerous changes in the polymer matrix material when the ionic liquid steps in [16]. The ionic liquids act as plasticizing agents in polymer/ionic liquid based ionogels making them flexible by weakening the polymer chains. The combination of ionic liquid and pressure treatment can help in generating pores in polymer based ionogels. The applied pressure can form interconnected pores in the membranes endowed with ionic liquid whereas membranes based on neat polymer cannot form pores on applying pressure due to mechanical strength. Moreover, the increasing content of ionic liquid results in the increased interaction between polymer and ionic liquid. In addition, the regions in the polymeric ionogel membranes that contain large amounts of ionic liquid have reduced mechanical strength and forms large sized pores [16]. These remarkable attributes of polymer/ionic liquid based ionogels allured scientists and researchers worldwide to further explore these ionogels for the welfare of mankind. Different kinds of polymers have been manipulated as the matrix material for the formation of ionogels like nylon [17], cellulose [18], poly(methyl methacrylate) (PMMA) [19], polyvinylidene fluoride (PVDF) [20], polyether sulfone (PES) [21], polypropylene (PP) [17] and polydimethylsiloxane (PDMS) [22]. Fig. 1 shows a simplified structural sketch of polymer based ionogels.

Amongst a large variety of polymers that are being exploited for synthesizing polymer/ionic liquid based ionogels, polyvinylidene fluoride (PVDF) has been highly emphasized. A large number of polyvinylidene fluoride (PVDF) based ionogels have been reported for a wide variety of applications. The polyvinylidene fluoride (PVDF) based ionogels display commendable properties by ionic liquids which serve as the major component of ionogels. In this review, the polyvinylidene fluoride

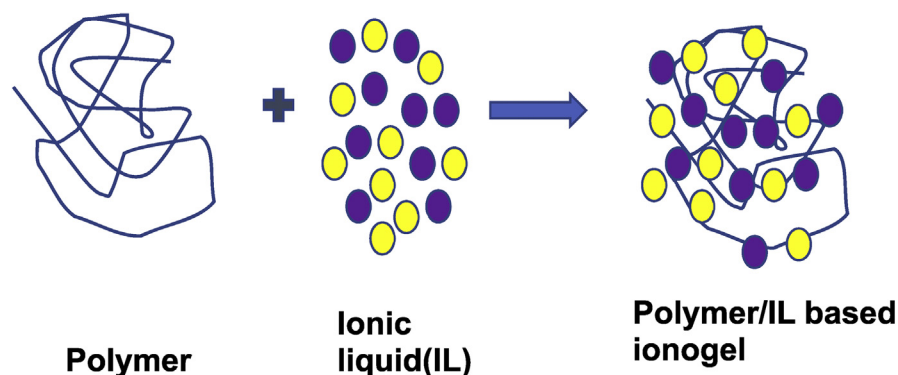


Fig. 1. Polymer based ionogels.

(PVDF) based ionogels and their applications in electrochemical devices and membrane separation have been discussed.

2. Ionic liquid, ionogels, properties and applications

2.1. Ionic liquids

Ionic liquids have recently appeared as a new class of compounds with many versatile and attractive properties. The ionic liquids essentially consist of ions defined as organic salts that exist in liquid state at temperatures lower than 100 °C. These ionic liquids are considered as alternatives for volatile organic solvents [23]. Some of the outstanding properties of ionic liquids that designates them as green solvents include in-flammability and their non-volatile nature. Apart from these some other captivating properties of ionic liquids includes their excellent ability of solvation [24], recyclability [25], thermal stability, tunable properties [26], and large electrochemical window [27]. A glance on historical perspective shows that ethyl ammonium nitrate ($[\text{C}_2\text{H}_5\text{NH}_3][\text{NO}_3]$) with melting point ~ 12 °C was the first ever ionic liquid that was synthesized by Paul Walden about ninety years ago [28].

An ionic liquid is composed of a cation and an anion. A cation is a less proportioned bulk organic structure where as an anion may be organic or inorganic in nature. The most notable and expansively used cations are based on pyrrolidinium, imidazolium, ammonium, sulfonium, picolinum, phosphonium and pyridinium whereas anions include $[\text{BF}_4]^-$, $[\text{SbF}_6]^-$, $[\text{PF}_6]^-$, $[\text{TF}_2\text{N}]^-$, $[\text{CF}_3\text{SO}_3]^-$ and alkyl sulfates etc. Some of the most commonly used cations and anions are shown in Fig. 2a and b. Columbic forces operate between cations and anions in an ionic liquid [28]. Ion pairs serve as the basic structural and repeating unit of ionic liquids. Electrostatic interactions exist among these ion pairs and are the basic cause of directionality of the interactions [29].

The properties of ionic liquids can be altered according to use and application. The properties of ionic liquids are deduced from the nature of anion and cation particularly their hydrophobic or hydrophilic character. An anion mostly determines the hydrophobicity or hydrophilicity of an ionic liquid [30]. Generally, the anions like BF_4^- , NO_3^- , ClO_4^- , methyl sulfate, pseudo halides and halides are hydrophilic whereas anions like PF_6^- , $[\text{C}_4\text{F}_6\text{SO}_3]^-$, bis(perfluoroalkyl)-imides are hydrophobic [31]. Moreover, the aromatic character of imidazolium cation also enhances the hydrophilicity of the ionic liquid [32].

The ionic liquids serve as potential candidates for various applications as shown in Fig. 3 such as separation [33], electrolytes [34], catalysis [35], fuel cells [36], dye sensitized solar cells (DSSCs) [37], tribology [38] and various chemical reactions [39, 40].

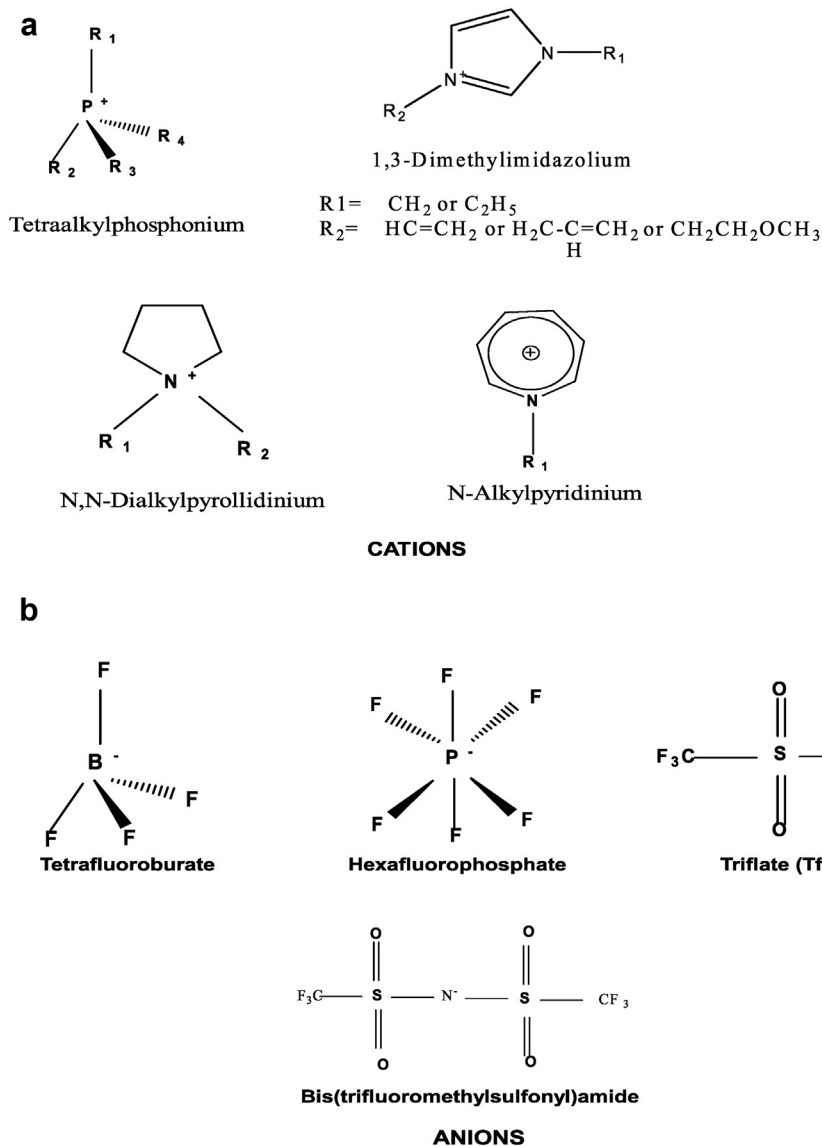


Fig. 2. Chemical structures of common (a) cations and (b) anions in ionic liquids.

2.2. Classification of ionogels

Based on the type of confining matrix, ionogels are classified into three major classes: Fig. 4 shows the different classes and sub classes of ionogels i.e. Inorganic ionogels, organic ionogels and hybrid ionogels.

2.2.1. Inorganic ionogels

Inorganic ionogels are defined as ionogels that are produced via gelation of an ionic liquid with silica or confinement of ionic liquids in conducting matrices or in oxide matrices [7].

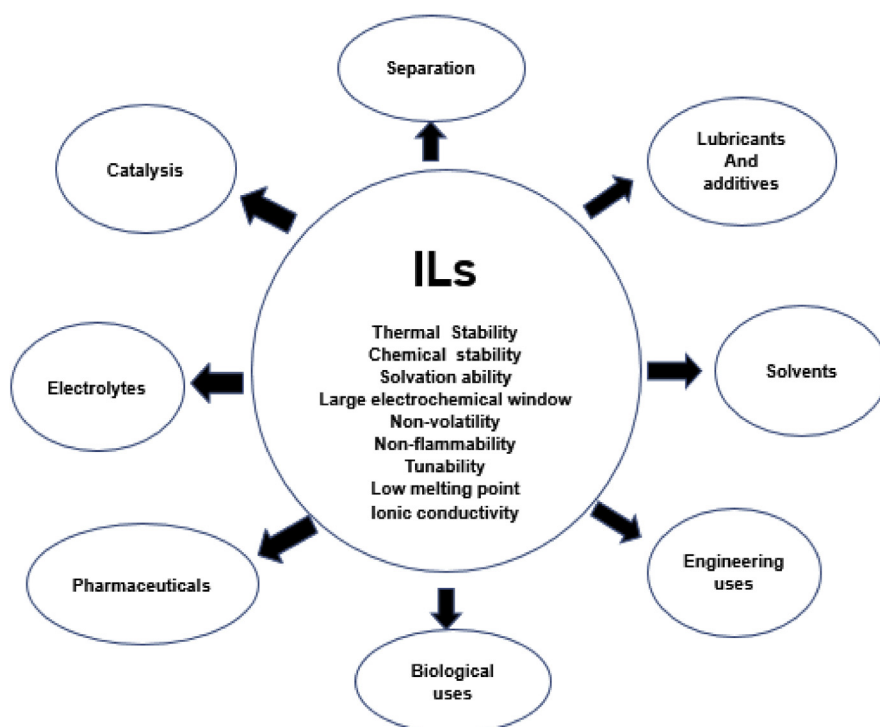


Fig. 3. Properties and applications of ionic liquids.

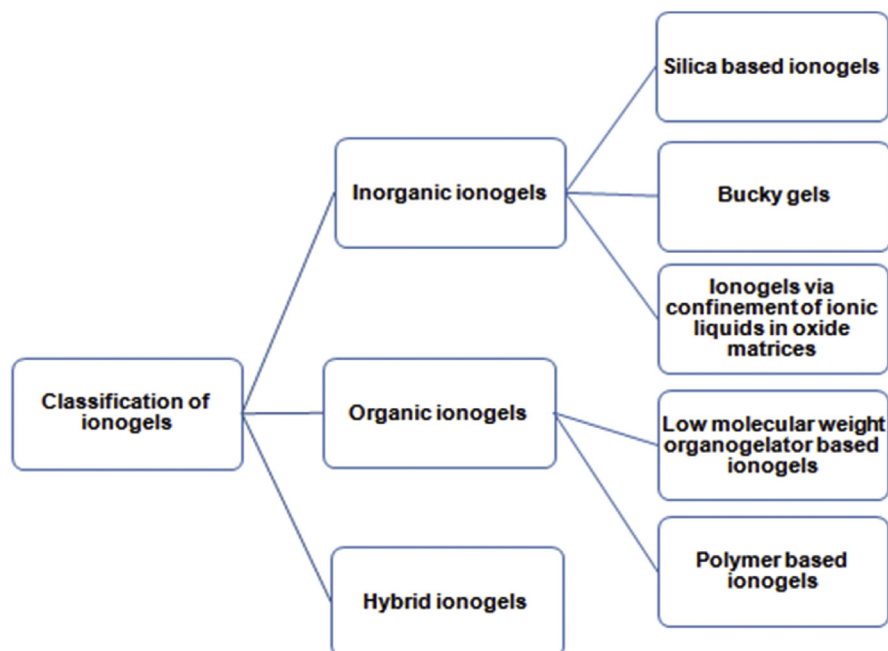


Fig. 4. Classification of ionogels.

Silica based ionogels involves either sol gel method or the dispersion of nano particles of silica for the synthesis of ionogels based on silica [7]. Horowitz et al. used an ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMI][TFSI]) for synthesizing ionogels based on silica. These silica based ionogels showed superior mechanical properties as compared to previously reported silica based ionogels [3].

Bucky gels can be precisely defined as soft gel like materials composed of ionic liquids and carbon nanotubes. The π -cation and π -anion electronic interactions are responsible for the formation of these bucky gels [41]. The carbon nanotubes are dispersed in ionic liquids due to inter ionic interactions. Resultantly physical cross links are established between the ionic liquid and carbon nano tubes leading to the formation of physical gels. The synthesis simply involves grinding in an agitate mortar or sonicating the carbon nanotubes and ionic liquids [41].

Confinement of ionic liquids in **nano porous oxide matrices** such as SnO_2 , TiO_2 etc. results in inorganic ionogels. These oxides serve as the gelating agent in the synthesis of these ionogels by using sol gel method [42]. Generally, metallic precursors are used for obtaining these inorganic ionogels. Liu et al. reported an ionogel based on an ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM] $[\text{BF}_4]$) and titania (TiO_2). The ionogels were used in actuators which were capable of working in harsh temperature environments [42].

2.2.2. Organic ionogels

Organic ionogels are defined as ionogels that are formed as a result of immobilization of ionic liquids in polymer matrices or by using low molecular weight organogelators (LMWOGs) [43].

Organic molecules that induce gelation in liquids are referred to as **low molecular weight organogelators (LMWOGs)**. These low molecular weight organogelators causes physical gelation in liquids and are added at high values of temperature in small quantities [7]. Low molecular weight organogelators lead to the formation of ionogels via incorporation of these low molecular weight organic gelators in an ionic liquid at an increased value of temperature followed by cooling Kubo et al. used a low molecular weight organic gelator designated as N-benzyloxy-carbonyl-1-isoleucyl and an imidazolium based ionic liquid for the synthesis of ionogels. The study revealed that the imidazolium based ionic liquids yield highest conversion efficiency [44].

The **polymer based ionogels** have used various polymeric materials for the synthesis of ionogels. Different routes have been adapted for the synthesis of these ionogels which may include in-situ polymerization, swelling a polymer in an ionic liquid or blending the ionic liquid and a polymer with a co-solvent [45]. Neil Winterton

et al. has worked on the polymer based ionogels and have stressed the ionic liquid functionality in the synthesis of polymer based ionogels. The ionic liquids have a tendency to furnish a medium for polymerization or to act as functional agents when incorporated in a polymer [46]. Yan et al. has reported polymer/ionic liquid based ionogel membranes based on protic ionic liquids. These polymer/ionic liquid based membranes were thermally, and chemically stable, transparent and flexible [47]. Some of the polymer based ionogels are described in the following Table 1:

2.2.3. Hybrid ionogels

Hybrid ionogels are defined as ionogels formed as a result of combination of polymer matrices, nano fillers and ionic liquids. Some methods for the preparation of hybrid ionogels include physical blending, sol gel method and incorporation of a latent organogelator.

Table 1. Polymer based ionogels and applications.

Polymer	Ionic liquid	Application	References
Polytetrafluoroethylene (PTFE)	<ul style="list-style-type: none"> Trihexyldecylphosphonium bis-2,4,4-trimethylpentylphosphinate (Cyphos 104) 	Removal of lactic acid from fermentation broth.	[48]
Polyethersulfone (PES)	<ul style="list-style-type: none"> 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) amide ([HMIM][Tf₂N]) 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl) amide ([OMIM][Tf₂N]) 	Separation of CO ₂ from gaseous mixtures of O ₂ , N ₂ and CH ₄ .	[49]
Polypropylene (PP)	<ul style="list-style-type: none"> Trioctylmethylammonium bis(trifluoromethylsulfonyl) imide ([OMA][NTf₂]) Trihexyl (tetradecyl) phosphonium bis(trifluoromethylsulfonyl) imide ([Ph₃t][NTf₂]) Trihexyl(tetradecyl)phosphonium dicyanamide ([Ph₃t][DCN]) 	Separation of 1-butanol from water.	[17]
Polyethersulfone (PES)	<ul style="list-style-type: none"> 1-Ethyl-3-Methylimidazolium bis(trifluoromethylsulfonyl) imide [EMIM][NTf₂] 1-Butyl-3-Methylimidazolium bis(perfluoroethylsulfonyl) imide [BMIM][BETI] 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF₄] 	Separation of CO ₂ from N ₂	[50, 51]
Polytetrafluoroethylene (PTEE)	<ul style="list-style-type: none"> 1-ethyl-3-methylimidazolium Dicyanamide [EMIM][DCA] 	Separation of CO ₂ from N ₂ .	[52]

Physically blending involves blending of polymer electrolyte, ionic liquid and inorganic nano filler physically [53]. Wang et al. has used the simple physical blending method for the synthesis of electrolytes. The synthesis of electrolytes was based on poly (vinylidene fluoride-co-hexafluoropropylene), silica nano particles and an ionic liquid 1-methyl-3-propylimidazolium iodide. The synthesis involved simple mixing, heating and sonication [53].

Sol gel method is a widespread method for the preparation of hybrid ionogels. The sol gel method is a very simple method which initially involves the suspension of the desired solid particles in a liquid medium forming a sol. In the next step, different methods like dipping, coating or spinning are used for deposition of the sol on a substrate. The sol is transferred in to a gel via incorporation of an initiator or by evaporation followed by heating [54].

The synthesis of hybrid ionogels via **introduction of a latent organogelator** lead to the formation of new class of ionogels designated as latent gel electrolyte precursor. These latent organogelators induce sudden gelation at high levels of temperature [55].

2.3. Properties of ionogels

2.3.1. Stability of ionogels

Stability is one of the most remarkable properties of ionogels. Ionogels are quite stable. In a magic angle spinning nuclear magnetic resonance (MAS NMR) rotor probe, even at 10 kHz centrifugation, the ionic liquid 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide ([BMIM][NTf₂]) was not expelled from the membrane based on silica. As far as immersion of ionogels in water is concerned, ionogels are stable as long as the ionic liquid used for the synthesis of ionogel shows no solubility in water. Moreover, stability for ionogels was observed in the organic solvents which are non-polar whereas the organic solvents which are polar in nature showed less stability [56]. It has been experimentally verified that ionogels are stable in hexane, toluene and water. However, these ionogels were unstable in chloroform and acetonitrile [57].

2.3.2. Mechanical properties of ionogels

The mechanical properties of ionogels are highly significant for their use in various applications. However, the incorporation of ionic liquids in different solid support materials affects their mechanical properties [58]. Lopez-Barron et al. has worked on the mechanical properties of ionogels. The mechanical properties of the synthesized polymer/ionic liquid based ionogels are highly affected by the cross-linking process [58]. The resistance to deformation as a result of applied mechanical stress is an important factor in determination of mechanical properties. While studying the

deformation resistance in cellulose/ionic liquid based ionogels impregnated with nano silica, it has been observed that the deformation resistance in response to applied mechanical stress increases with an increasing content of nano silica. This has been attributed to the increase in density of three dimensional networks formed in the ionogels upon incorporation of nano filler [58].

2.3.3. Thermal properties of ionogels

Thermal stability is one of the outstanding features of ionogels which credits to the thermal stability of ionic liquids [58]. Saroj et al. has synthesized polymer/ionic liquid based ionogels by using Poly (vinyl) pyrrolidone (PVP) and an ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF₄]). The cellulose/ionic liquid based ionogels with nano silica as a nano filler were synthesized and their thermal behavior have been analyzed. It was concluded that ionogels based on nano fillers were thermally more stable as compared to the simple composite ionogels [58]. In a study conducted on ionogels based on low molecular weight organogelators (LMWGs), it was revealed that these ionogels are thermo reversible. These ionogels melt when heated and again becomes gel when cooled [59].

2.3.4. Conductive properties of ionogels

The ionic liquids impart appreciable conductive properties to the ionogels. The interaction between polymer matrix and ionic liquid facilitates filling of high ionic liquid content without leaking out from ionogel. Ionogels based on nano fillers such as graphene have been investigated and it was found that that the ionic conductivity increases with the addition of these filler [60].

2.3.5. Applications of ionogels

As discussed earlier, ionogels have been widely employed in various applications. Some possible applications of ionogels included electrochemical, catalysis, solar cell, actuators, fuels cell capacitors, medicine and etc [55, 56, 57, 58, 59]. For electrochemical devices, the conductivity of material containing IL should be ≥ 1 mS/cm [44]. This is due to the reason that IL has conductivity in the range of 0.1–20 mS/cm which maintains a comparable level of conductivity in ionogels [48]. For energy applications, Ionogels based membranes are typically used as solid polymer electrolytes (SPE). Because SPE are those gel electrolytes which contain IL that not only serves as charge carriers but also as plasticizers [35, 36, 37, 38]. Ionogels for energy application includes electrolytic membranes, Li-ion batteries, dye-sensitized solar cells and fuel cells [40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52]. Ionogels have also been used for formation of inkjet-printed microstructures [53]. ILs have ability to dissolve a range of materials such as organic compounds, metal salts and gases. This property makes ionogels a superior candidate for separation

processes of gases: the rate of transport and selectivity depends on the type of the polymer membrane [44, 45]. IL containing ionogels have also been reported in the field of catalysts. They offer superficial entrapment of nanoparticles, improved performance, and protective atmospheres for biocatalysis [39]. One of the fascinating applications are actuators such as intelligent robots, electrochemical sensors and biosensors [58]. This is due to their unique structure containing ionically conductive electrolyte inserted between two electrically conductive electrodes, which under the applied voltage allows the redistribution of different sizes of cations and anions [10, 58, 59, 60, 61]. Another application of application of ionogels can be drug delivery with the purpose to reduce drug degradation and loss hence preventing harmful side effects and increase in drug bioavailability [55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67].

2.4. Polyvinylidene fluoride based ionogels

A large number of based ionogels have been reported. The polyvinylidene fluoride (PVDF) based ionogels have a broad range of utilization and have been divided in different categories herein, depending on the nature of application. Polyvinylidene fluoride (PVDF) serves as a significant example of thermoplastic polymers awarded with some noteworthy properties like resistance to aging and chemicals, high mechanical strength, thermal stability and electro activity with $-(\text{CH}_2\text{CF}_2)_n-$ as its repeating structural unit. The polymer also exhibits piezoelectric, ferroelectric and pyroelectric features. Furthermore, there exists five different phases of polyvinylidene fluoride namely α , β , γ , δ and ϵ -phase. α -phase is non-polar and is formed from molten polyvinylidene fluoride (PVDF) whereas β -phase results from incorporation of nano fillers or by mechanical stretching. β -phase is the most extraordinary phase in terms of applications and it shows highly elevated levels of piezoelectric properties. These properties make polyvinylidene fluoride (PVDF)/ionic liquid based ionogels a broadly investigated class of polymer/ionic liquid based ionogels.

There exists electrostatic interactions between the polymer and ionic liquid in polyvinylidene fluoride (PVDF)/ionic liquid based ionogels and these interactions are stronger than the plasticization effect created by the ionic liquid [61]. In contrary to pure polyvinylidene fluoride (PVDF) which shows non-polar α -phase and electroactive β phase, the polyvinylidene fluoride (PVDF)/ionic liquid based ionogels shows only electroactive β phase in some cases. The incorporation of ionic liquids in polyvinylidene fluoride (PVDF) encourages the formation of β and γ forms of the polymer [20, 62].

2.4.1. Electrochemical devices

The low vapor-pressure and inflammable nature of ionic liquids presents a number of advantages including safety and higher operating temperatures yielding them

extremely useful for electrochemical devices [63]. Additionally, the excellent conductive properties shown by ionogels also make them widely investigated composite materials for use in electrochemical domains. A large variety of polymer based ionogels have been used for this purpose [64]. Fig. 5 highlights some of the properties and applications of polyvinylidene fluoride (PVDF) based ionogels in electrochemical devices.

The use of different ionic liquids has different effects on conductive properties of ionogels. The conductivity of ionogel based on an ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF₄]) was found to be greater than that of ionogel based on an ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIM][OTf]) [65]. Moreover, the presence or absence of solvent has no effect on conductivity [65]. Similarly, the incorporation of filler may or may not affect the conductivity of ionogels. For example, the addition of zeolite didn't affect the conductivity of ionogel based on ionic liquid 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide ([EMIM][Tf₂N]) [66]. However, ionogels based on ionic liquid 1-ethyl-3-methyl imidazolium tetrafluoroborate ([EMIM][BF₄]) showed a decrease in conductivity with the addition of zeolite [66].

The polyvinylidene fluoride (PVDF) based ionogels form electrochemically stable, elastic, flexible, non-volatile and conductive electrolytes [67]. Hence, the ionogels

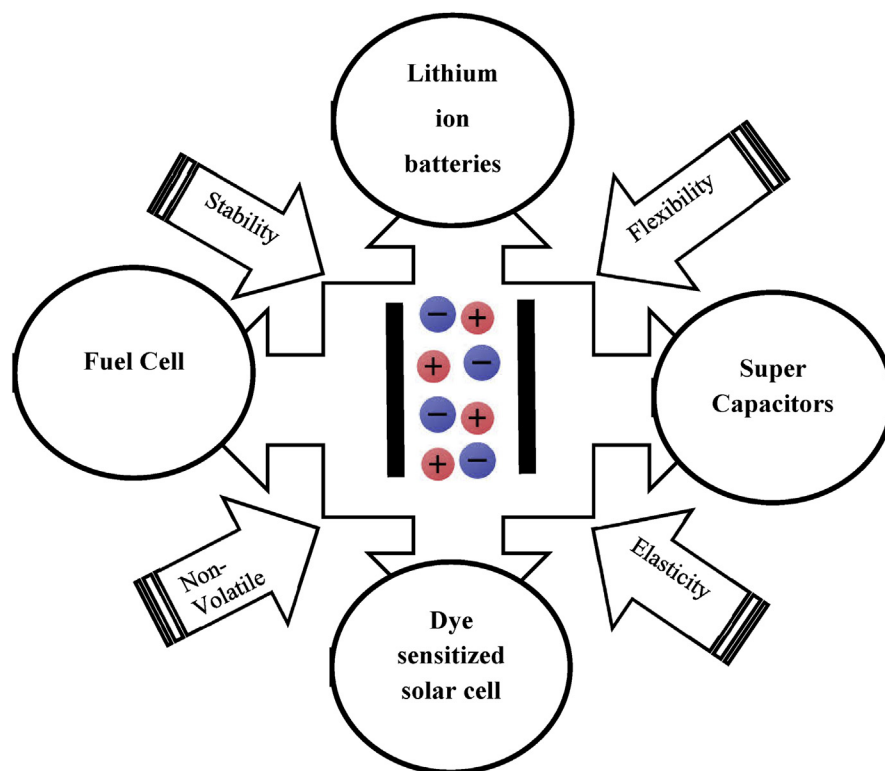


Fig. 5. Polymer based ionogels for electrochemical devices.

based on poly (vinylidene fluoride)-hexafluoropropylene (PVDF-HFP) have been reported for use in *lithium batteries* [67]. Addition of ethylene carbonate in small amounts highly affects the conductivity. Similarly, these electrolytes are in *fuel cells* [68]. The electrolyte thus synthesized has also been used as an electrolyte material for separating the electrodes in the *super capacitor* [69].

2.4.2. Membrane separation

Ionic liquids have been successfully implemented in the separation of a wide range of gases and liquids in the form of polymer/ionic liquid based ionogel membranes [70]. The polymeric membranes based on ionic liquids have noticeable effects on selectivity, permeability and transportation. These membranes have a wide range of applications in separation of gasses and liquids [71]. The separation mechanism as well as some important properties of ionogel based membranes is shown in Fig. 6.

The applicability of this polyvinylidene fluoride (PVDF) based ionogels in gas separation and liquid/liquid separation is given below:

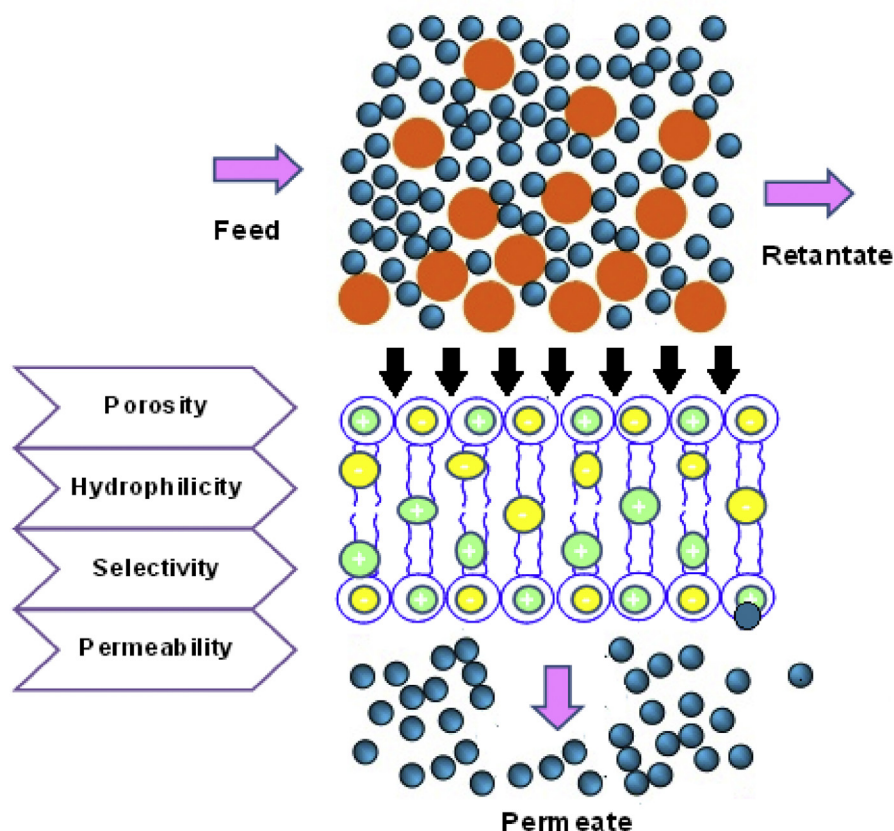


Fig. 6. Polyvinylidene fluoride based ionogels for membrane separation.

2.4.3. Gas separation

The solubility and absence of contamination contributes to a large-scale use of these polyvinylidene fluoride based ionogel membranes in gas separation. The tailor able nature of ionic liquids renders them more selective for a particular gas as compared to another gas [72]. Moreover, as discussed earlier, the constituent cations and anions determine the properties of ionic liquid. Hence different ionic liquids have different properties and consequently different effects on separation efficiency of membranes [73]. For example, the polyvinylidene fluoride (PVDF) based ionogel membranes for separation of gaseous mixtures composed of carbon dioxide (CO₂) and nitrogen (N₂) containing 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonfyl) imide ([BMIM][Tf₂N]) showed maximum permeability whereas the membranes containing 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) displayed least permeability [73]. Similarly, polyvinylidene fluoride (PVDF) based ionogel membranes have been reported for the separation of bio-hydrogen. The greatest value of permeability was attained with the membranes containing 1-octyl-3-methylimidazolium hexafluorophosphate ([OMIM][PF₆]) [74].

The hydrophobic polyvinylidene fluoride (PVDF) based membranes impregnated with room temperature ionic liquid (RTIL) based on 1-n-alkyl-3-methylimidazolium cation forms stable membranes [75]. Moreover, an increase in the length of alkyl chain of cation of room temperature ionic liquid (RTIL) is consistent with an increase in the permeation of gasses and an increase in the viscosity of room temperature ionic liquids (RTILs) leads to a decrease in permeability. These ionogels were then used in the separation of gaseous mixtures composed of carbon dioxide/nitrogen (CO₂/N₂) and carbon dioxide/methane (CO₂/CH₄) [75].

Another significant aspect in the study of polyvinylidene fluoride (PVDF) based ionogel membranes in gas separation is the effect of amount of gas and physical conditions on separation efficiency. The study of polyvinylidene fluoride (PVDF) based ionogels for the removal of carbon dioxide (CO₂) from a mixture of carbon dioxide (CO₂) and nitrogen (N₂) revealed that the permeability of carbon dioxide (CO₂) was decreased with greater amounts of carbon dioxide (CO₂) and pressure difference [76]. The application of polyvinylidene fluoride (PVDF) based ionogels in gas separation are given in Table 2.

2.4.4. Liquid/liquid separation

The polyvinylidene fluoride (PVDF) based ionogel membranes are also substantially useful for liquid/liquid separations. The polyvinylidene fluoride (PVDF) based ionogel membranes containing ionic liquids Trioctylmethylammonium chloride (Aliquat 336), Trihexyltetradecylphosphonium chloride (CyphosIL-101), Trihexyltetradecylphosphonium bromide (Cyphos IL-102), were most suitable for recovery of lactic acid

Table 2. Polyvinylidene fluoride based ionogels for gas separation.

Polymer	Ionic liquid	Application	Reference
Polyvinylidene fluoride (PVDF)	<ul style="list-style-type: none"> 1-methylimidazolium acetate [MIM][ace] 1-Butylimidazolium acetate [BIM][ace] 	Transportation of carbon dioxide (CO ₂) and sulphur dioxide (SO ₂)	[77]
Polyvinylidene fluoride (PVDF)	<ul style="list-style-type: none"> 1-butyl-3-methylimidazolium dicyanamide [BMIM][DCA] 	Separation of three gases including carbon dioxide(CO ₂), Oxygen (O ₂) and nitrogen(N ₂)	[78]
Polyvinylidene fluoride (PVDF)	<ul style="list-style-type: none"> 1-butyl-3-methylimidazolium hexafluorophosphate [C₄MIM][PF₆] 1-octyl-3-methylimidazolium hexafluorophosphate [C₈MIM][PF₆] 1-butyl-3-methylimidazolium tetrafluoroborate [C₄MIM][BF₄] 1-decyl-3-methylimidazolium tetrafluoroborate [C₁₀MIM][BF₄] 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide [C₄MIM][Tf₂N] 	Separation of gaseous mixtures composed of carbon dioxide/nitrogen (CO ₂ /N ₂) and carbon dioxide/methane (CO ₂ /CH ₄)	[75]
Polyvinylidene fluoride (PVDF)	<ul style="list-style-type: none"> 1-butyl-3-methylimidazolium acetate [Bmim][Ac] 1-ethyl-3-methyl imidazolium acetate [Emim][Ac] Vinyl benzyl trimethylammonium acetate [Vbtma][Ac] 	Separation of carbon dioxide (CO ₂) from nitrogen (N ₂)	[79]

from fermentation broth [80]. The polyvinylidene fluoride (PVDF) based ionogels are durable and stable which accounts for their large-scale use in liquid/liquid separations. The polyvinylidene fluoride (PVDF) based supported ionic liquid membranes (SILMs) for the separation of organic liquids were long-lasting [80]. These supported ionic liquid membranes (SILMs) have also been employed in the removal of rare earth elements from the magnetic scrap [82]. The incorporation of ionic liquid in these polyvinylidene fluoride (PVDF) based membranes also significantly affects the permeability, diffusion co-efficient and the flux rate. Ionic liquids tend to act as plasticizing agents in polymer based ionogel membranes [83]. Polyvinylidene fluoride (PVDF) based polymer inclusion membranes (PIMS) have been reported for separation of Cr (VI) which revealed that the ionic liquid plasticizers (ILPs) significantly affect the permeability co-efficient of the membranes [71]. Similarly, these polyvinylidene fluoride (PVDF) based ionogels for the recovery of ethyl acetate from water revealed an increase in the diffusion co-efficient and flux rate [83]. Table 3 highlights some applications of polyvinylidene fluoride (PVDF) based ionogels in liquid/liquid separation.

Table 3. Polyvinylidene fluoride based ionogels for liquid/liquid separation.

Polymer	Ionic liquid	Application	Reference
Polyvinylidene fluoride (PVDF)	• Trioctylmethylammonium chloride Aliquat336	Elimination of lactic acid from fermentation broth.	[80]
	• Trihexyltetradecylphosphonium chloride CyphosIL-101		
	• Trihexyltetradecylphosphonium bromide CyphosIL-102		
	• Trihexyldecylphosphonium bis-2,4,4-trimethylpentylphosphinate CyphosIL-104		
	• Trihexyltetradecylphosphonium bis-trifluoromethylsulfonyl imide Cyphos-IL-109		
	• Trihexyltetradecylphosphonium tetrafluoroborate Cyphos IL-111		
Polyvinylidene fluoride (PVDF)	• 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF ₆]	separation of organic liquids.	[81]
Polyvinylidene fluoride (PVDF)	• 1-octyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide [C ₈ mim][Tf ₂ N]	removal of rare earth elements from the magnetic scrap	[82]
Polyvinylidene fluoride (PVDF)	• 1-ethyl-3-methylimidazolium methyl sulfate	Separation of thiols	[84]
	• 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide		
	• 1-ethyl-3-methylimidazolium tri flate		
Polyvinylidene fluoride (PVDF)	• 1-n-decyl-3-methylimidazolium hexafluorophosphate, C10imPF ₆	Separation of organic compounds	[85]
	• 1-n-butyl-3-methylimidazolium hexafluorophosphate, bmimPF ₆		
	• 1-n-butyl-3-methylimidazolium tetrafluoroborate, bmimBF ₄		
	• 1-n-octyl-3-methylimidazolium hexafluorophosphate, C8imPF ₆		

3. Conclusions

In this review article, the polyvinylidene fluoride (PVDF) based ionogels and their applications in various fields have been discussed. The classification of ionogels and their methods of synthesis have also been stressed. Ionic liquids have been declared as the major constituent of this polyvinylidene fluoride (PVDF) based ionogels and their structural, physico-chemical features and applications have been highlighted. Additionally, polyvinylidene fluoride (PVDF) has been discussed as the choicest material for the synthesis of ionogel based membranes which credits to the remarkable properties of this polymer. The polyvinylidene fluoride (PVDF) based ionogels have found applications in diverse range of applications including electrochemical devices and separation membranes. The properties of these ionogels can be further

modified by the incorporation of nano fillers especially carbon based nano fillers including reduced graphene oxide (RGO), nano diamonds, carbon nanotubes (CNTs), graphene and carbon black which paves way for research in this domain in future.

Declarations

Author contribution statement

All authors listed have significantly contributed to the development and the writing of this article.

Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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