Ionic Liquid-Based Hybrid Materials: Ionogel Review

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Abstract: Ionic liquids (ILs) are gaining popularity due to their unique qualities, which include low vapor pressure, thermal stability, and non-flammability, as well as strong ionic conductivity and a wide electrochemical stability window. Ionogels (IGs) are solid electrolytes that are based on ionic liquid (IL). Incorporation/entrapment of ILs in any inorganic or organic solid host material results in the formation of IGs. Furthermore, to develop lithium-ion batteries (LIBs) with high capacity, high rate capability, and outstanding cycle stability, this paper focuses on clever methodologies for synthesizing organic, inorganic, and hybrid host-based IGs. In this review, ionogels are described as a novel type of hybrid material in which the characteristics of an IL are combined with those of another component, which can be organic (low molecular weight gelator, biopolymer, etc.) or inorganic (carbon nanotubes, silica, etc.) or a hybrid organic-inorganic (e.g., polymer and inorganic fillers.

Keywords: ionic liquids; solid electrolytes; ionogel; batteries.

1. Introduction

Ionic liquids (ILs) are organic salts with a low melting point, usually below 100 degrees Celsius. They are made up entirely of ions and have very different characteristics from those of ionic liquids. Non-flammability, thermal stability, and vapor pressure are some of the most significant characteristics. The ionic pair can be used to adjust the choice of anion-cation pair [1]. Because of their excellent conductivity and large electrochemical potential window, ILs have been frequently utilized by electrochemists for a long time. The current need for electrochemical devices like actuators, lithium batteries, and fuel cells has sparked a renewed interest in high-performance electrolytes. They provide good performance throughout a wide temperature range (usually up to 200–300 °C) [2]. This is owing to the fact that these materials must be able to resist temperatures between 200 and 300 degrees Celsius. Organic solvents (ILs) are used in a variety of industrial applications, such as catalysis and extraction [3]; there is gaining interest as a substitute for organic molecules (VOCs). The chemical industry has taken notice of ILs because of their unusual mix of non-volatility and favorable solubilizing properties. The usage of ILs looks sustainable, and they have been labeled as "green" solvents [4]. The question of whether or not ILs are environmentally beneficial is now being debated. Nonetheless, biomolecules have lately been used to create benign ILs. Organometallic compounds and biocatalysis are in the realm of homogeneous catalysis [5]. There has been a lot of work done in the field of organic nanomolecules in recent years, particularly in the research of biocatalysts. It has been shown to be a novel reaction medium, particularly in the field of metal electrodeposition [6]. They can dissolve both inorganic and organic species.

Although its usage in inorganic chemistry is relatively recent, it is not a long-standing issue. Many studies have been done on the controlled growth of nanoparticles in ILs, especially metal nanoparticles, and their catalytic activity in organic processes. An evaluation of the use of ILs in manufacturing a range of inorganic materials was carried out [7].

The unique structural and physicochemical properties of ILs have led to their increasing application in the materials industry [8]. Ion aggregates are formed, which are stabilized by ionic interactions, hydrogen bonds, and van der Waals forces [9]. The physicochemical characteristics of ILs, serve as the foundation for all IL-based applications. The first section of this article is organized as a rough sketch of the new knowledge of structures and their potential applications. Immobilizing ILs in solid devices while maintaining their unique characteristics is difficult. One option is to impregnate support, the IL, as an adsorbed film for this purpose. The creation of supported IL is a good example of this technique, known as supported IL catalysis (SILC). SILC involves immobilizing metal catalysts within IL films, resulting in free-flowing powders ideal for continuous fixed-bed reactors. IL is a technique for immobilizing the body by forming ionogels, which are solid-like substances [10]. The ionogel is also known as ion gel. Physical and chemical gels can be differentiated from ionogels. In physical gels, weak (reversible) interactions involving hydrogen bonds, hydrophobic interactions, and covalent bonding cross-link the interior 3-D network [11]. Chemical gels vary from physical gels in that they generate cross-links due to covalent bonding. Physical gels are frequently in the form of jellies and slurries or have limited mechanical firmness. Another option is to make chemical gels by trapping the IL in a network of covalently linked molecules. The presence of IL may have a significant impact on the structural and textural characteristics of organic matrices. Sol-gel cross-linking of covalently bound oxide nanofillers is a third method [12].

Ionogels are predicted to have characteristics that differ from those of an IL and a solid-like network. In organic polymers built on polymers, only one transition is seen at a temperature (Tg) lower than that of the pure polymer but higher than that of the pure IL [13]. The confinement effects found in inorganic ionogles are even more specific. They might be caused by a confinement in the host matrix's nanopores.

Ionogels, which have all of the characteristics of ILs except for outflow, have a far broader range of uses [14]. Solid electrolytes, medication release, and catalysis are just a few examples. The ability to functionalize designer molecules by encapsulating them in the immobilized IL phase is limitless. Ionogels can also be employed as detergents to make them more resistant to chemical reactions (figure 1) [15].
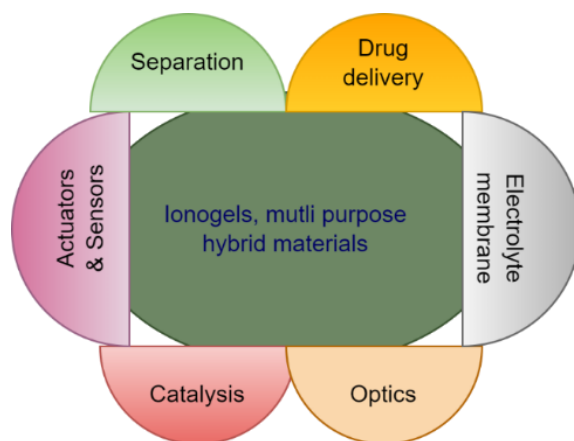

Figure 1. Ionogels.

2. Structure and Physicochemical Characteristics of ILs and their Relationships

Organic cations like phosphoniums, pyridiniums, and imidazolium are used in aprotic ILs [16]. Aprotic cationic ionic liquids (CILs) result from a proton transfer to the same location as an alkyl group. Protic ILs have much greater fluidities and associated conductivities than aprotic ILs. This is owing to their higher hydrophilicity, which allows them to form more easily than aprotic ILs. Protic may also be able to resist high temperatures, resulting in improved ionic stability. Although ILs are made using very basic organic chemistry, their purification is far from easy, as distillation and crystallization are not readily available. Then, minor quantities of contaminants were shown to have a significant impact on their characteristics. This article gives a quick overview of ongoing efforts to rationalize the fundamental physicochemical properties of water-stable and air-stable ILs. Ionic association in ILs might not be able to contribute to the material's conductivity. This is because all ions must be neutral. They were unable to help with the low vapor pressure.

Commonly used cations:
- alkyl- 3- methyl- imidazolium
- N- alkyl- pyridinium
- Tetraalkyl ammonium
- Tetraalkyl phosphonium

Some anions in increasing order of their water miscibility:

PF6 -, BF4 -, OTf-, CH3COO-, NO3-,Br-, Cl-, CF3COO-

Preparation of ionogels:

Depending on the nature of the solid-like network, inorganic ionogels (ionogels) can be produced in three distinct methods (figure 2).
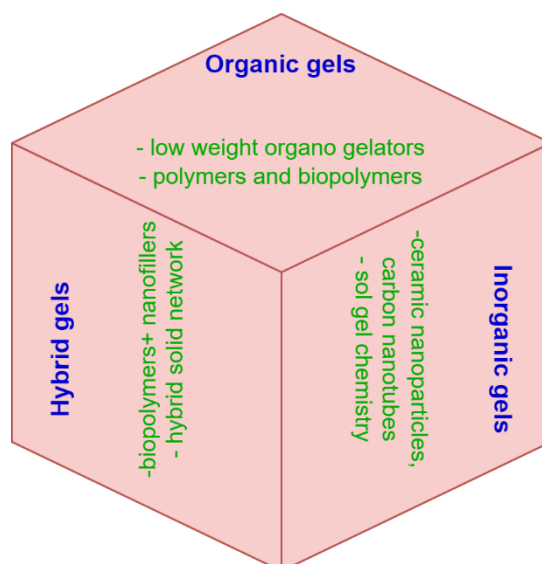

Organic gels
- low weight organo gelators
- polymers and biopolymers

Hybrid gels
-biopolymers+ nanofillers
- hybrid solid network

Inorganic gels
-ceramic nanoparticles, carbon nanotubes
- sol gel chemistry

Figure 2. Different types of ionogels.

3. Organic Ionogels

Low molecular weight gelators (LMWGs) are organic compounds introduced to liquids in small amounts at high temperatures and subsequently cause physical gelation when the liquid cools [17]. Supramolecular bonds, including hydrogen bonding, p–p interactions, and electrostatic interactions, allow them to self-assemble in solution. Adding L-glutamic acids or carbohydrates to ether-containing ILs can be gelled [18]. The presence of b-D-glucose and a-

cyclodextrin was discovered. Strong interactions between carbohydrates and ether groups resulted in the formation of fibrous nanostructures. Pi-stacking, van der Waals interactions, and metal-metal bonding were shown to be involved in gelation [19]. The first organometallic gelator, a pyridine-bridged bis (benzimidazolylidene)-palladium complex, was shown to be effective in the gelation of many ILs [20].

4. Polymer Gels

Polymers have been employed to immobilize ILs in various applications, including electrochemical devices [21]. Many gelled systems may be produced by simply swelling a polymer or mixing the polymer and the IL with a co-solvent and then withdrawing the co-solvent [22]; the essential element is the IL's miscibility with the polymer. Many ILs have been discovered to act as plasticizers, lowering the glass transition temperature and allowing for greater flexibility [23].

By utilizing poly (benzyl methacrylate) and its copolymer PBzMA as a porogen solvent, the capacity of poly (benzyl methacrylate) and its copolymer PBzMA to self-assemble in the presence of an IL may be utilized [24]. In rare circumstances, employing IL as a solution might result in cross-linked resins with persistent macro porosity [25]. Some ionogels produced from tri-block copolymers have been demonstrated to display phase separation in polymer thin-film transistors when exposed to external stimuli (such as temperature) [26]. Cellulose is a polymer that, microwave at 120–170°C, dissolves in water-soluble chloride and may be regenerated in water. Gelation happens when the IL solution is kept at room temperature for a few days in a humidified environment. Cellulose may also be utilized as a biopolymer to create cellulose gels that can be mixed with agarose or carrageenans [27].

5. Inorganic Ionogels

Bulky gels: Carbon nanotubes ('Bucky' tubes) have remarkable mechanical, electrical, and thermal characteristics, yet they're difficult to work with. Aida and Fukushima discovered in 2003 that single-walled carbon nanotubes (SWNTs) might be distributed readily in imidazolium ILs. The resulting 'Bucky gels' are simple to mold into any form. Because they combine electro-conductive CNTs and ion-conductive ILs, this has opened up a wide range of uses [28].

6. Silica-based Ionogels

Silica-based ionogels can be made by dispersing silica nanoparticles in ILs or using a sol-gel method [29].

6.1. Dispersion of silica nanoparticles.

Graetzel was the first to use the gelation of ILs in the presence of silica nanoparticles to generate thermally stable quasi-solid electrolytes [30]. Honma examined the ionic conductivities of gels produced with 10% [C4MIm] [TFSI], proving the importance of particle size in gelation. This gelation led to the formation of a dense particle network, suggesting that the particles had only a modest repulsive contact, which was insufficient to stabilize them [31].

6.2. Sol-gel processing.

S. Dai *et al*. reported the first sol-gel synthesis in an IL solvent, using a combination of tetramethoxysilane (TMOS) and formic acid in [C4MIm] to make silicas with large surface areas [32]. Actually, the IL was utilized as a template after it was removed after the synthesis. The influence of ILs as drying control chemical agents was blamed for forming a non-volatile liquid layer on the walls of pores [33]. An ionogel with a very strong and highly monochromatic red photoluminescence was created by doping a europium (III) nn tetrakis b-diketonate complex into an imidazolium IL and immobilizing the IL in a silica-like network. This method allows for the inclusion of any metal complex (even those sensitive to formic acid), which opens the door to a broad range of applications, including sensors and displays [34].

7. Inorganic Matrices Oher than Silica

Dionysiou and his colleagues at the University of Paris explored the hydrolytic sol-gel method, which produces highly porous titanium oxide particles with anatase crystalline structure from a titanium isopropoxide precursor at room temperature in the presence of water [35]. The researchers discovered that they had steady ion conductivities throughout a wide temperature range, including the 100–200 °C intermediate region.

8. Composite Ionogels

The interaction between molecular organogelators and inorganic nanoparticles has received little attention. The latent gelators in the gel electrolyte precursors were silica or titania nanoparticles and a dicarboxylic acid (usually with a C16 chain). The precursor crystallized into a dye-sensitive dye-sensitized solar cell (DSSC) after being baked at 80 °C [36].

Clays and silica can be employed as compatibilizers between polymer chains and polar inorganic fillers like imidazolium ILs. This is a means of counteracting the plasticizing impact of large IL loadings while keeping the resultant nanocomposite materials flexible and tractable [37]. Inorganic nanoparticles are commonly utilized to enhance the mechanical characteristics of polymer ionogels. The usage of ILs in various ternary polymer/inorganic filler/IL systems illuminates the potential function of ILs.

9. Effects of Detention

While glass transition is observed in silica ionogels at all degrees of confinement, there is no evidence of cold crystallization or melting at the greatest confinement levels. This is due to the chemical composition of both pore and crystal structure having a major influence. The smallest shift recorded with ILs is higher than that found with molecular liquids (contrary to viscosity). In the case of ILs, the melting point of the liquid-substrate affinity on transition temperature is proportional to the degree of confinement. As the temperature rises, the IL system shifts from a rigid lattice to more dynamic phenomena associated with the diffusive state. This shift is followed by a narrowing of the NMR signal lines, which is typical of the melting point in the case of crystalline salts and at the glass transition temperature for amorphous materials [38].

On monolithic silica ionogels, 1H NMR spectra of confined IL revealed a very narrow signal without spinning. This showed that even with liquid-like mobility, the dipole-dipole and chemical shift anisotropy could be averaged [39]. Due to the susceptibility gradient at the

surface wall neighborhood, a spinning rate as low as 400 Hz was sufficient to restore liquid-like resolution, but the signal was not as narrow as for bulk IL [40].

The ionic conductivity of rigid porosity silica ionogels is of interest. Using CIS, the ionogel demonstrated conductivity of the same order of magnitude as bulk IL. The shifts of the bands assigned to n (CH2) revealed some variations in the conformational order of the chain in the case of imidazolium ILs with long alkyl chains. As a result, the conformation was disordered compared with the bulk crystalline solid IL at room temperature [41].

An anion–anion arrangement resulted from a particular configuration of the ions in the wall neighborhood, which led to this unexpected fluorescence increase [42]. When comparing the europium (III) complex dissolved in an IL contained in a silica matrix to that dissolved in bulk IL, it was discovered that the europium (III) complex dissolved in an IL confined in a silica matrix was around 200 times stronger than that of bulk [C4MIm] ionogel. This demonstrated that confinement had no effect on the structure of the europium (III)-doped IL structure [43]. There was no discernible difference in degradation times (confined IL vs. bulk), confirming the confined IL's liquid-like behavior.

10. Applications

10.1. Electrolytic membranes.

In order to build improved energy devices, luxuriant inorganic molecules (ILs) are of great interest. In proton-exchange-membrane fuel cells (PEMFC), ILs can substitute traditional media, organic solvents in batteries, or water in non-flammable ILs [44].

10.2. Lithium-ion batteries.

Lithium batteries are projected to play a significant part in renewable energy plants and sustainable cars as electrochemical storage devices. Researchers may consider the present development of all-solid IL-based lithium batteries a true milestone in the area. The primary disadvantage of LiNi1/3Mn 1/3Co1/2Co1 /3O2-based electrodes is their slow-cycling rate (C/20 at RT). This is due to the electrode material's reduced solubility in the IL-polymer electrolyte. Compared to this cathode material's capacity in standard electrolytes, a battery using LiV3O8 as the positive electrode and PEO-PVdF contained IL-based electrolytes showed a (slight) increase (figure 3) [45].

10.3. Fuel cells.

To deliver more efficient power production and a longer lifetime, PEMFCs require high temperatures for operation. The selection of proton-conducting ionic liquids (PCILs) has been the subject of extensive investigation. PCILs can be used as proton carriers in fuel cell electrolytes, allowing for conductivities of more than 10 mS cm-1 in completely anhydrous circumstances [46].

In liquid-based nanocomposites, a team of researchers from the University of California, San Diego, discovered a reduction in ionic conductivity and viscosity [47]. They tried to boost proton conductivity with super acids like trifluoromethanesulfonic acid (N,N-bis), but it didn't work. The primary disadvantage of such a membrane is the possibility of cracks, which would "short-circuit" the gas route. A recent study on silica-derived ionogels

based on silicon-based ionosilane was published, although more than one side of the chemical reaction cannot be made up (figure 4).
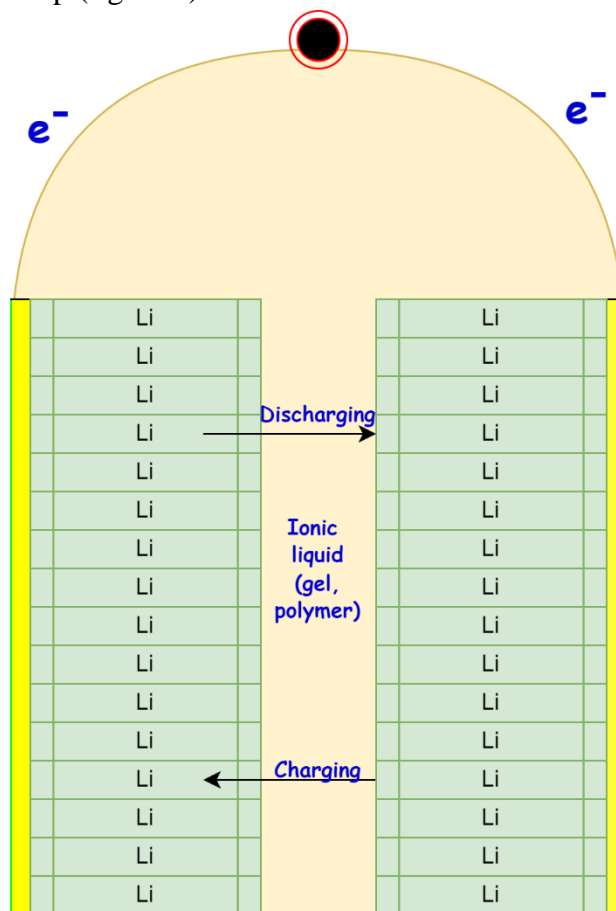

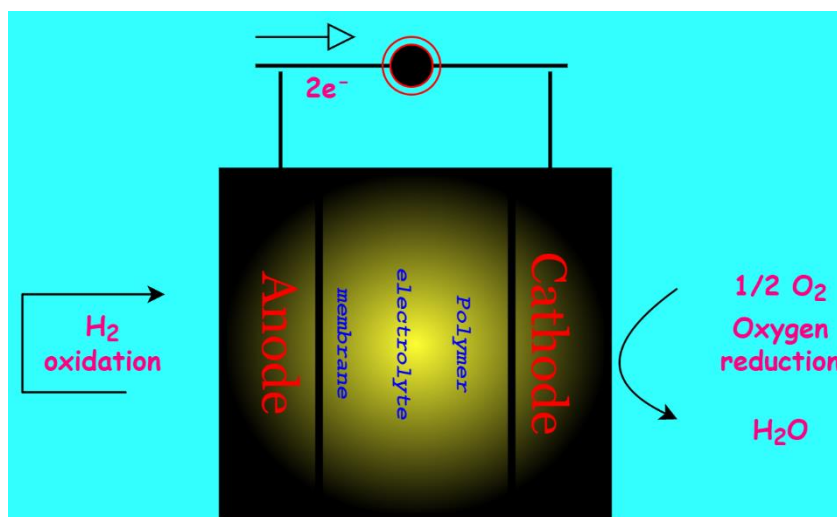**Figure 3.** All-solid IL-based lithium battery.

Figure 4. IL-based polymer electrolytes fuel cells.

10.4. Solar cells.

Physical gels made by combining silica nanoparticles as a "gelator" to solidify IL-based electrolytes (with the addition of KI and I2) resulted in improved dye-sensitive solar cell performance (DSSCs). Using a ruthenium polypyridyl photosensitizer, such ionogels were applied to DSSCs, resulting in a 7 percent efficiency (figure 5) [48].
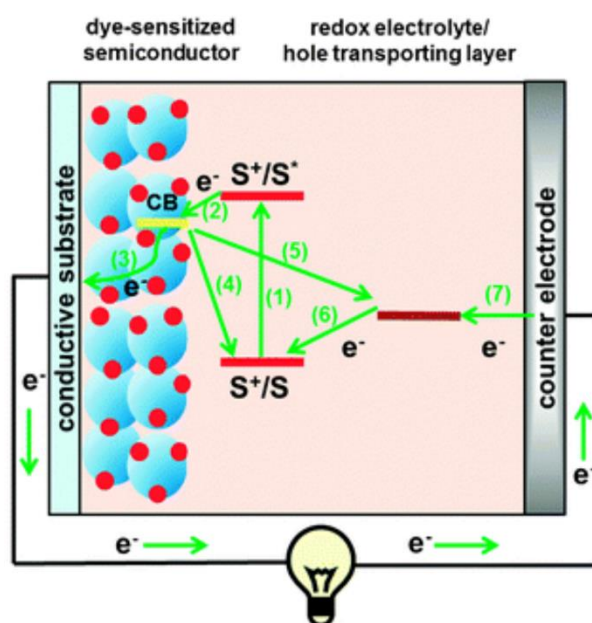
Figure 5. All-solid dye-sensitized solar cell.

10.5. Electrochemical sensors and biosensors.

Coll *et al*. revealed how to make anion-selective electrodes out of PVC membranes containing bis (trifluoro methane sulfonimidate) and poly aza cycloalkane as ionophores [49]. They discovered that the extremely hydrophilic anion sulfate elicited a surprising selective response. Even in the presence of ascorbic acid and uric acid, the researchers were able to detect dopamine selectively [50].

Actuators: Aida *et al*. published the first generation of Bucky-gel actuators in 2005, which operated in the absence of any support or external electrolytes, as well as a metallic electrode layer. The layer-by-layer casting of the electrode from a combination of a fluorinated copolymer (PVdF-HFP), 4-methyl-2-pentanone, an IL, and SWCNTs resulting from high-pressure CO conversion was used to create the film [51].

10.6. Separation membranes.

The solubility of gases in ILs is critical if they are to be used as reaction solvents. The unique characteristics of ILs extend the spectrum of separation applications, from metal ion separations to chromatography. They're also useful for separating organic substances like organics and metals. In gas separation, polymerizable IL (IL) has been demonstrated to improve selectivity over traditional polymer membranes [52]. This was due to the IL being displaced at low differential pressure. However, this problem was solved by combining polymerizable IL with 20 mol percent free room temperature ionic liquids (RTILs). These customized membranes enabled gas separation with a 400% increase in CO_2 permeability and improved CO_2/N_2 and CO_2-selectivity [53].

10.7. Catalytic membranes.

Alternative nano reactor systems have been shown using silica-based ionogels. The existence of two interconnected networks (silica and IL) enables unrestricted movement of reactants and products through the liquid phase, with pore sizes small enough to avoid IL

leaching. Deng *et al.* found the carbonylation of aniline into ureas and carbamates in the presence of silica-based ionogel [54].

10.8. Drug release.

Ionogels are being used for drug release for the first time. It is based on ionogels that can gradually lose IL instead of being stable under operational circumstances. The in situ delivery of the IL loading into the body is referred to as drug release. Recently, several efforts have been made to develop nontoxic and biodegradable ILs. These new IL medicines have a lot of potential over usual solid active pharmaceutical ingredients (APIs), which can suffer from low solubility and low bioavailability. Therefore, the pharmaceutical industry is putting in much effort to create medication delivery methods that allow the active material to be released 'on demand.' When compared to most organic polymers, microbial attack, silica matrices have greater biocompatibility–biodegradability, and resistance to microbial attack, as well as improved mechanical strength, enhanced thermal stability, and minimal swelling in organic solvents [55].

11. Conclusions

Ionogels are a new type of hybrid material that is only getting started, but they have a lot of promise in areas including energy, the environment, and analysis. Both the cation and anion components' characteristics can be changed separately. The unusual chemical and physical characteristics of ionogels provide another dimension to this "flexibility space."
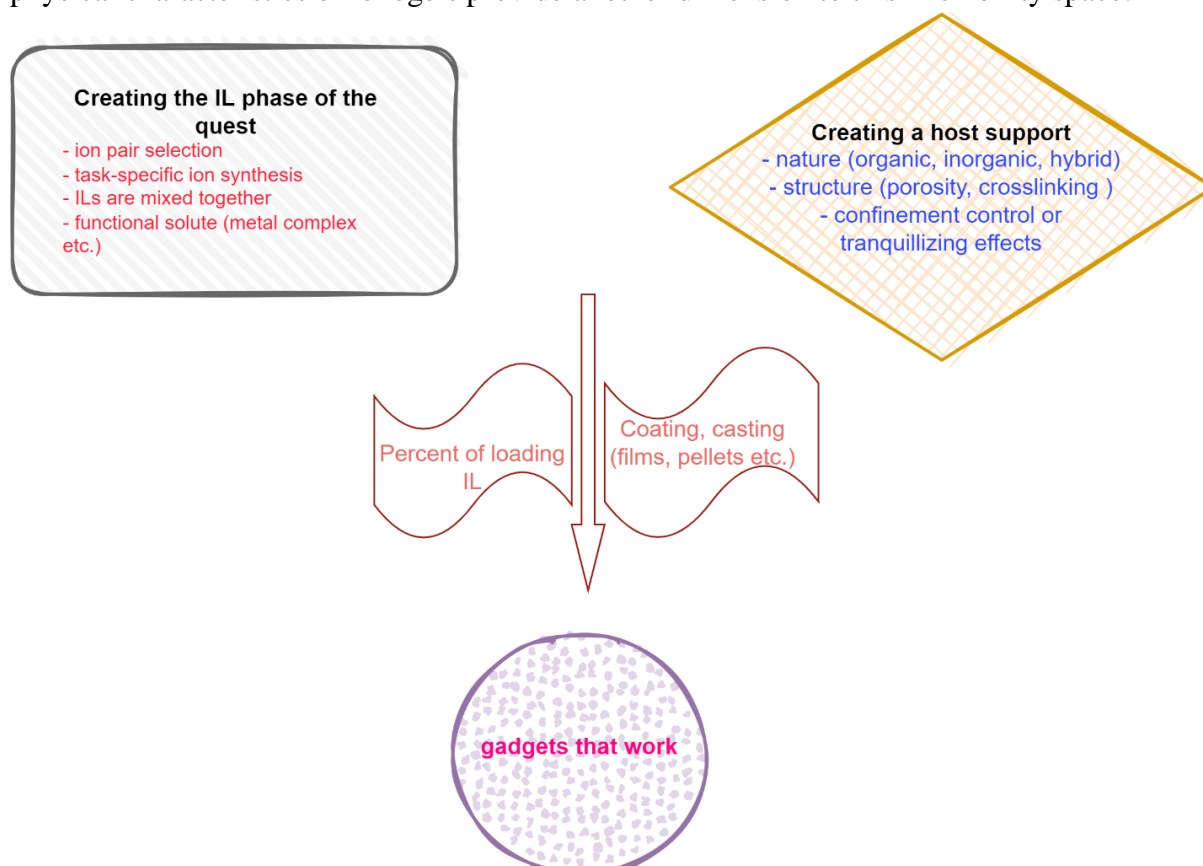

Figure 6. Ionogels, tailored hybrid materials.

By exploiting the compatibility of the IL with the polymer or the inorganic phases that form during in situ syntheses, inorganic ionogels may be shaped at the nanometer scale. The

nanostructure and physicochemical characteristics of the IL may be altered when it is immobilized in the host matrix. This is attributed to a short-range organization and molecular dynamics change in the pore wall's immediate vicinity. The structure then freezes before evolving into macroscopic phase separation on its own. The notion of ionogel offers up an infinite number of applications and should stimulate creative, most likely surprising technological advances in the future (figure 6).

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Conflicts of Interest

The authors declare no conflict of interest.

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