

Engineering Encapsulated Ionic Liquids for Next-Generation Applications

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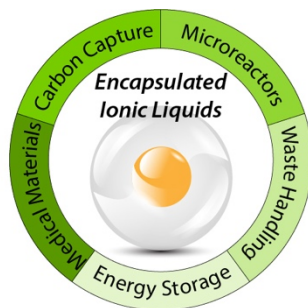
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Abstract

Ionic liquids (ILs) have attracted considerable attention in several sectors (from energy storage to catalysis, from drug delivery to separation media) owing to their attractive properties, such as high thermal stability, wide electrochemical window, and high ionic conductivity. However, their high viscosity and surface tension compared to conventional organic solvents can lead to unfavorable transport properties. To circumvent undesired kinetics effects limiting mass transfer, the discretization of ILs in small droplet has been proposed as a method to increase the effective surface area and the rates of mass transfer. In the present review paper, we summarize the different methods developed so far for encapsulating ILs in organic or inorganic shells and highlight characteristic features of each approach, while outlining potential applications. The remarkable tunability of ILs, which derives from the high number of anions and cations currently available as well as their permutations, combines with the possibility of tailoring the composition, size, dispersity, and properties (*e.g.*, mechanical, transport) of the shell to provide a toolbox for rationally designing encapsulated ILs for next-generation applications, including carbon capture, energy storage devices, waste handling, and microreactors. We conclude this review with an outlook on potential applications that could benefit from the possibility of encapsulating ILs in organic and inorganic shells.

Table of Content (Graphical Abstract)



Keywords: ionic liquids; encapsulation; carbon capture; energy storage; waste handling; microreactors.

1. Introduction

Ionic liquids (ILs) are a class of organic salts that consist of cations and weakly coordinating anions.¹⁻⁴ The low melting temperature of ILs, which is close to or even below room temperature, is the result of the difference in size of anions and cations as well as the charge delocalization and geometric asymmetry of (at least) one of the ions. The unique properties of ILs (*e.g.*, high thermal stability, low flammability, wide electrochemical window, low vapor pressure, and high ionic conductivity) have made them candidate materials for several applications, including as electrolytes in energy storage devices,⁵ additives in lubricants,⁶ and separation media.⁷ One particularly attractive feature of ILs is their tunability: owing to the number of permutations of cations and anions, ILs can be designed and synthesized with task-specific properties, which has led to consider ILs as “designer solvents”.²⁻⁴

The broad applicability of ILs has resulted in a continuously growing number of published papers related to their investigation (Figure 1). In the case of studies exploring the potential use of ILs as electrolytes for energy storage devices, adsorbed layers on solid catalysts, or lubricants, significant efforts have been spent in evaluating the structure and dynamical evolution of solid/IL interfaces as they determine the functional behavior (*e.g.*, charge storage of supercapacitors, friction reduction).⁸⁻²² The confinement of ILs in nanoscale geometries creates radically different conditions than the ones in the bulk phase, and promotes a strong interaction with the boundaries of the confining matrix, which affects the behavior of ILs (*e.g.*, phase transition, wetting, and ion mobility).^{19,21,22}

In the case of studies aiming to use ILs as separation or reaction media, the high viscosity and surface tension of these fluids compared to conventional organic solvents can lead to unfavorable transport properties. To circumvent undesired kinetics effects limiting mass transfer, ILs have been supported on solids to combine the advantages of using ILs as solvents with the ones of solid-based technologies²³. These early efforts focused on the stabilization of ILs on a variety of solid supports, such as porous silica²⁴⁻²⁶, membranes^{23,27}, and electrolytes²⁸. Recently, the discretization of ILs in small droplet has been proposed as a method to increase the effective surface area and mass transfer rate.^{24,29-40} Since the first report demonstrating the possibility of encapsulating ILs within microcapsules, several research groups developed methodologies for discretizing ILs in microscopic particles with engineered transport properties. In light of the numerous developments reported in the literature, this review article aims to provide an overview

on the methodologies developed so far for encapsulating ILs, the criteria for their selection (Section 2), and the application of encapsulated ILs (Section 3). This contribution ends with a perspective about potential future applications of encapsulated ILs (Section 4).

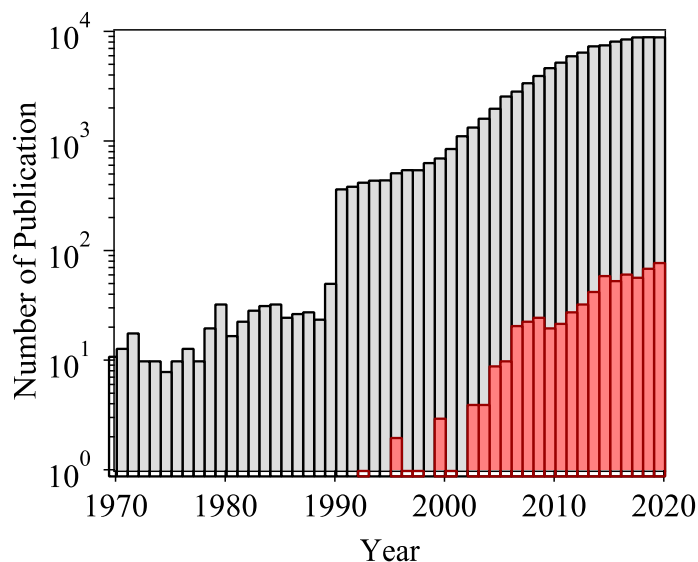


Figure 1. Number of publications per year that include “ionic liquid” (black bars) or “encapsulated ionic liquid” (red bars) in the title, abstract, or keywords (data obtained from Web of Science in February 2021).

2. Methods of Encapsulation

Several methods for encapsulating ILs within a shell made of a second material have been reported in the literature. Table 1 lists the different methods together with details about the encapsulated ILs, the shell material, and the size distribution of the capsules. Figure 2 displays schematics for each method presented below.

Table 1. Methods for encapsulating ionic liquids (ILs) within an organic or inorganic shell. Details about the encapsulated IL, shell composition, and size distribution of the microcapsules are also provided. The chemical structures of cations and anions constituting the ILs are, respectively, reported in Table A.1 and Table A.2 in the Appendix.

<i>Encapsulation Method</i>	<i>Ionic Liquid</i>		<i>Shell Type</i>	<i>Size Distribution (μm)</i>	<i>Ref.</i>
	<i>Cation</i>	<i>Anion</i>			
Emulsion Polymerization	[BMIM]	[TFSI]	Poly(butyl methacrylate-co-ethylene glycol dimethacrylate)	5-15	41
	[HMIM]	[TFSI]			
	[BMIM]	[PF ₆]	Polyurea	2-80 (average: 22)	42
	[BMIM]	[PF ₆]	Silica	4-5	32
	[BMIM]	[PF ₆]		2-14 (average: 7)	43
	[P _{6,6,6,14}]	[(C ₈) ₂ PO ₂]		0.3-1	44
	[EMIM]	[TFSI]		100-250	45
	[HMIM]	[TFSI]	Poly(thiourethane) and poly(amide-thioether)	60-200	
Impregnation	[OMIM]	[PF ₆]	Activated Carbon	0.45	37
	[P _{6,6,6,14}]	[2-CNPyrr]		0.31-0.53	46
	[BMIM]	[OAc]		0.34	47
	[EMIM]	[NTf ₂]		0.9±0.1	48
	[N _{H2,Me,EtOH}]	[Pe]			
	[EtOHmim]	[BF ₄]			
	Choline	[NTf ₂]		0.6	49
	[(EtOH) ₃ MeN]	[MeSO ₄]			
Pickering Emulsion	[P _{6,6,6,14}]	Cl	Sodium alginate/gelatin	~2000	31
	[BMIM]	[PF ₆]	Reduced graphene oxide	25-100	50
	[BMIM]	[PF ₆]	Polyurethane/Lignin	From 27±18 to 105±25	51
	[BMIM]	[PF ₆]			
	[EMIM]	[TFSI]	Graphene oxide and polyurea	10-35	52
	[HMIM]	[TFSI]			
	[Mpp]	[TFSI]			
	[BM ₂ IM]	[PF ₆]			
	[EMIM]	[DMP]			
	[BMIM]	[BF ₄]		10-25	
	[EMIM]	[TFSI]			
				5-55	53

	[HMIM]	[TFSI]	Alkylated graphene oxide and polyurea	3-38	
Solvent Evaporation	[BMIM]	[PF ₆]	Polysulfone	170-300	30
	[EMIM]	[TFSI]		50-225	54
	[HMIM]	[TFSI]		5-25	55
	[BMIM]	[PF ₆]		44.2	35
	[BMIM]	[PF ₆]	Polyacrylonitrile	200-350	39
	[BMIM]	[BF ₄]			
	[HMIM]	[BF ₄]			
	[BMIM]	[TFSI]	Polystyrene	2	56
Vapor Phase Deposition	[EMIM]	[BF ₄]	Poly(tetrafluoroethylene) + Poly (1H,1H,2H,2H-perfluorodecyl acrylate-co-ethylene glycol diacrylate)	2000	38
Non-solvent induced phase inversion	[EMIM]	[TFSI]	Poly(vinylidene fluoride-co-hexafluoropropylene)	1000-2000	57
Chemical patterning	[BMIM]	Cl	Octadecyltrichlorosilane	1-1.5	58

Specific characteristic of the capsules should be considered when designing and fabricating them, including: (a) capsule size distribution; (b) chemistry of the shell material; (c) shell thickness; and (d) shell properties (*e.g.*, permeability, mechanical properties). The tunability of the capsules' chemistry, size, and properties provided by the synthetic approaches listed above combines with the versatility in combining varied cation-anion moieties (10^{18} ILs theoretically available)⁵⁹ to pave the way towards the rational design of encapsulated ILs with task-specific properties for a variety of applications in several sectors (Section 3). In the following, the most widely used encapsulation methods are briefly presented and discussed.

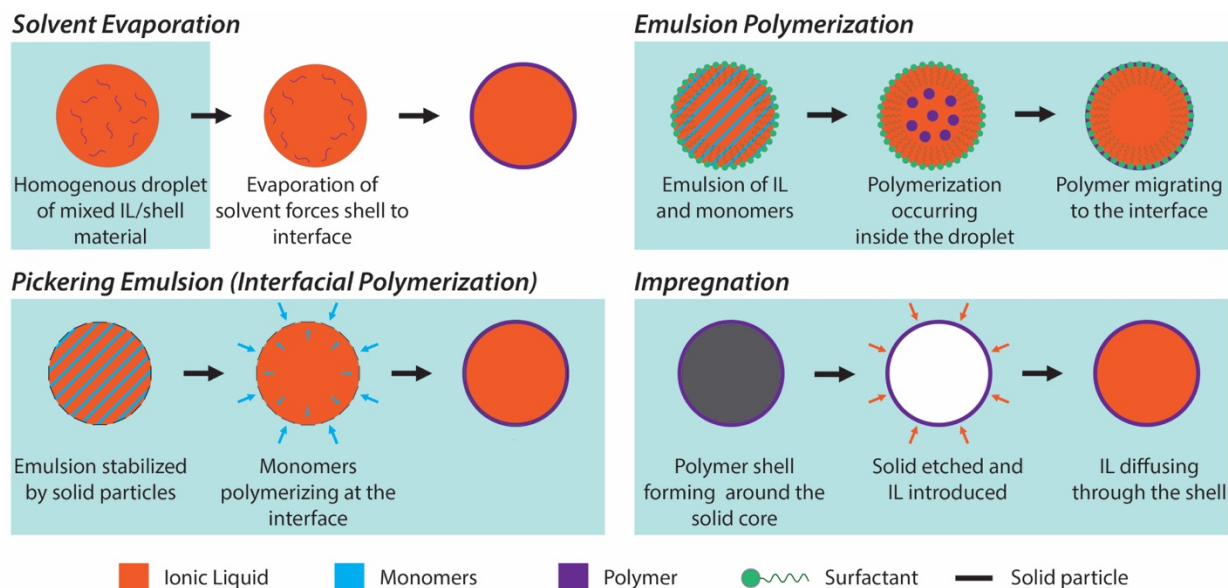


Figure 2. Schematic representations of the different methods used for the preparation of encapsulated ILs.

2.1. Emulsion Polymerization

One of the most common methods of forming microcapsules across all types of materials is based on the process of emulsion polymerization,^{60–65} in which a polymer shell is formed at the liquid/liquid interface of an emulsion. The fundamental mechanisms of microemulsion polymerization have widely been explored and characterized. As a particular example, Loxley and Vincent⁶⁶ provided a detailed discussion of the mechanisms and phenomena governing the formation of poly(methylmethacrylate) microcapsules with liquid cores. Compared to simpler solvent evaporation methods of capsule preparation (described in the following section), in emulsion polymerization the shell material is chemically bonded, typically via polymerization or cross-linking, once it is introduced to the emulsion interface. This enables complex formulations of shell materials, as component monomers can be added through both the disperse and continuous phases⁴². Because of this, the materials selection process is less restrictive relative to solvent evaporation. Additionally, the plethora of polymeric materials currently available paves the way towards the systematic evaluation of changes in shell chemistry/structure on functional properties (e.g., gas permeability, mechanical properties), while providing opportunities for shell optimization.

As the creation of an IL microemulsion in a continuous phase is the first step in the preparation of polymeric microshells with IL core, particular attention should be paid in the

parameters affecting the properties of the microemulsion. Recently, Hejazifar *et al.*⁶⁷ exhaustively reviewed the types, mechanisms of formation, and applications of IL microemulsions. One notable feature of IL emulsions that was highlighted is their tunability and possibility of including long alkyl chains in the ions, which make them amphiphilic and allowing them to function as surfactants able to stabilize the microemulsion.

One specific class of encapsulation methods of IL microemulsions was described by the Minami group as an extension of the self-assembly of phase-separated polymer method⁴¹, which is based on the authors' previous work with conventional oil in water microemulsions^{68–70}. In this method, the majority of the shell is formed by crosslinking ethylene glycol dimethacrylate (EGDM), though addition of polymethacrylates to the emulsion was shown to dramatically improve the internal capsule morphology. Figure 3 displays an example of scanning electron microscopy (SEM) and transmission electron microscopy (TEM) micrographs of cross-sections of the prepared poly(triethylene glycol dimethacrylate/n-butyl methacrylate)/poly(n-butyl methacrylate)/[HMIM][TFSI] (P(TEGDM-BMA)/PBMA)/[HMIM][TFSI]) composite particles, which exhibit a smooth surface morphology together with a single hollow inner structure.

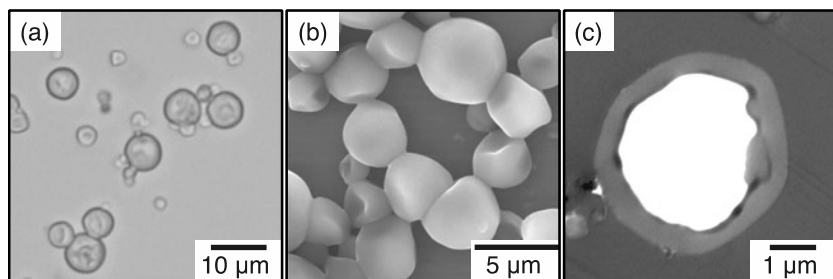


Figure 3. Optical micrograph (a), SEM (b), and TEM micrograph of ultrathin cross-section (c) of poly(triethylene glycol dimethacrylate/n-butyl methacrylate)/poly(n-butyl methacrylate)/[HMIM][TFSI] (P(TEGDM-BMA)/PBMA)/[HMIM][TFSI]) composite particles prepared by microemulsion polymerization. [Reprinted with permission from 41. Copyright (2013) Springer]

Though most preparations of IL capsules via emulsion are based on an aqueous continuous phase, IL-in-oil emulsions have also been produced.⁶⁷ An example of capsules created using an IL-in-oil emulsions was recently reported by Li *et al.*⁴⁵, who used poly(amide-thioether) as surfactant and exploited the IL (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [EMIM][TFSI], and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

[HMIM][TFSI]) to catalyze an IL/oil interfacial reaction and create a shell made of polythiourethane and poly(amide-thioether). Weiss *et al.*⁴² encapsulated 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) in polyurea microspheres by emulsification of [BMIM][PF₆] in oil and interfacial polymerization of isocyanate and amine polymers, while also highlighting the changes necessary in the surfactant when carrying out the emulsification in oil vs. in water. Even though surfactants were adjusted depending on the continuous phase (oil or water), the capsule morphology and size distributions were mostly similar (Figure 4).

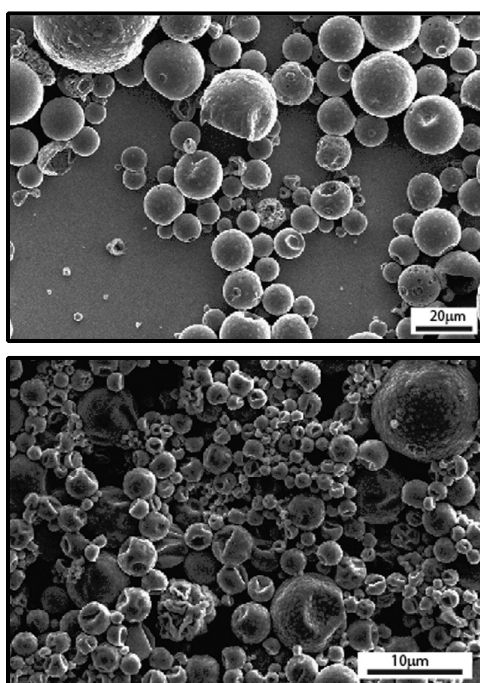


Figure 4. SEM micrographs of [BMIM][PF₆] in polyurea capsules prepared via emulsion polymerization in water (top) and in oil (bottom). [Reprinted from *React. Funct. Polym.*, Weiss, E.; Gertopski, D.; Gupta, M. K.; Abu-Reziq, R. Encapsulation of Ionic Liquid BMIm[PF₆] within Polyurea Microspheres. **2015**, 96, 32–38, with permission from Elsevier]⁴²

Finally, while microemulsion encapsulation has mostly been used to create polymeric shells, sol-gel condensation methods have also been employed to encapsulate ILs in solid capsules made of silica.^{32,43,44} This is typically achieved by direct addition of tetraethoxysilane (TEOS) to

an IL emulsion prepared using organic surfactants tailored to the IL-water interface^{32,44} or dissolved gelatin, similar to that used in preparations utilizing solvent evaporation⁴³.

Even though encapsulation via microemulsion polymerization is relatively straightforward and has great potential for further optimization owing to the tunability of the shell material enabled by our detailed knowledge of polymer chemistry, which allows several physico-chemical properties (*e.g.*, permeability) and mechanical properties of the polymeric shell to be tailored for specific applications, a significant drawback observed with this fabrication method is that capsule sizes tend to be highly polydisperse, and none of the permutations of this method performed so far has managed to consistently generate capsule with diameters less than 5 μ m. This limitation can greatly affect the potential use of encapsulated ILs due to negative impacts on capsule packing and long-term stability in suspensions.

2.2. Solvent Evaporation

Encapsulation via solvent evaporation is one of the simplest and most direct methods of microcapsule preparation, and thus was one of the earliest methods utilized for IL encapsulation. This class of encapsulation methods has remained popular for its simplicity due to the high miscibility of ILs and most organic solvents. The driving mechanism for capsule formation is the evaporation of a volatile solvent containing both the IL and the shell material, resulting in self-organization of the mixture based on relative interfacial energies. The primary shell material selected for IL encapsulation has been polysulfones (PSFs),^{30,54} due to their solubility in both ILs and volatile solvents such as dichloromethane (DCM), and the ability to form durable, IL-impermeable shells without further polymerization or crosslinking.

A potential major advantage for solvent evaporation is the relative ease of integrating microfluidic fabrication, and its associated advantages. As microfluidics have already been applied in the field of microencapsulation owing to the possibility of achieving monodisperse populations of microparticles of different size and shapes,^{71–75} several published studies have explored the possibility of encapsulating IL via solvent evaporation using microfluidics devices.^{30,39,76} Yang *et al.* used solvent evaporation to create hollow PSF microcapsules containing [BMIM][PF₆] IL using a two-stage microfluidic method,³⁰ while Xiang *et al.* used a microfluidic device to create an emulsion from a mixture of poly(dimethylsiloxane) and *n*-butyl acetate as continuous phase and a dispersed phase made of polyacrylonitrile and ionic liquids ([BMIM][PF₆], [BMIM][BF₄],

[HMIM][BF₄]) dissolved in *N,N*-dimethylformamide, which was followed by the extraction of *N,N*-dimethylformamide to create the microcapsules.³⁹ While the microfluidic technology provides the possibility of accurately controlling the size and distribution of the microcapsules, the encapsulation of IL through simple mechanical stirring could also be achieved, as demonstrated by Li *et al.*, who synthesized PSF microcapsules filled with [EMIM][TFSI] IL.⁵⁴

Among the methods described in this section, the solvent evaporation approach is the most conducive to large scale fabrication of encapsulated ILs, as the simple nature of the process combined with the possibility of precisely controlling the capsule size, which is enabled by the use of microfluidic devices, can allow for the production of relatively large quantities of capsules while minimizing variation within and between batches. However, the range of possible capsule compositions is relatively narrow, as the IL, shell material, and any potential additives must all be miscible (while mutually immiscible) with the carrying fluid.

2.3. Pickering Encapsulation

The use of Pickering emulsions (*i.e.*, emulsions stabilized by solid particles) as template for the encapsulation of ILs was pioneered by the group of Pentzer.^{50,52,53,77,78} This methodology, which employ either graphene oxide (GO) nanosheets or alkylated GO as surfactants, has two main advantages over other encapsulation methods: (a) the drastic reduction in the loading of the surfactant (in Pickering emulsions the surfactant/IL weight ratio is around $\sim 1/100$, while in the case of systems relying on molecular surfactants this ratio is $\sim 1/10$); and (b) the use of GO-based surfactants enables both IL-in-water and IL-in-oil emulsions to be created, thus allowing the selection of the most appropriate continuous phase for the IL under consideration. The latter advantage is particularly important in the case of ILs (most ILs are hygroscopic) as the possibility of performing the encapsulation in a water-free continuous phase enables the water content in the encapsulated IL to be carefully controlled. The selection of the GO-based surfactant strongly depends on the nature of the continuous phase: in the case IL-in-water systems, GO nanosheets stabilize the emulsions, while in the case of IL-in-oil systems the functionalization of GO nanosheets with alkyl amines of varied chain length can be used to stabilize the emulsions (Figure 5).⁷⁷

The stabilized Pickering emulsions could then be used as template for the formation of polymeric capsules via interfacial polymerization, in which the reaction occurs between reagents

present both in the IL and in the continuous phase (water or oil). Most polymerization reactions have been carried out using di-isocyanates and diamines as the monomers are commercially available and the reactions do not result in the formation of byproducts. The resulting capsules incorporate a large amount of IL (65-85 wt.%).^{50,51}

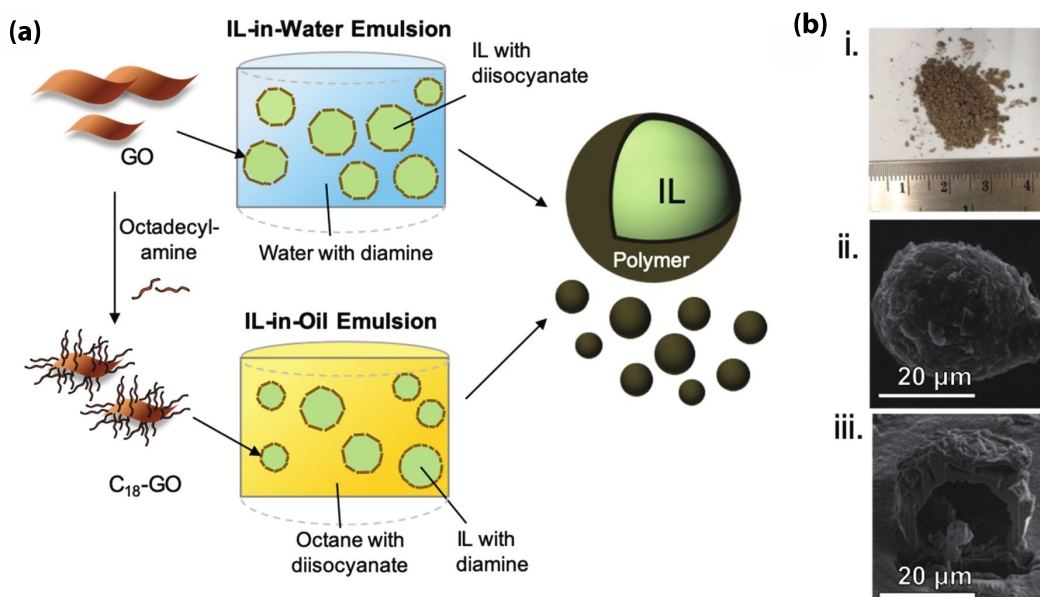


Figure 5. (a) Schematic representation for the preparation of encapsulated IL using either IL-in-water or IL-in-oil Pickering emulsions stabilized by GO nanosheets or alkylated GO nanosheets followed by interfacial polymerization; (b) photograph (i) and SEM micrographs ((ii) and (iii)) of ILs capsules. [Reprinted with permission from 52. Copyright (2019) American Chemical Society].

2.4. Impregnation

The high affinity of ILs with activated carbon (AC)⁷⁹ inspired Palomar *et al.* to encapsulate IL within carbon nanocapsules having a micro/mesoporous shell structure and a hollow core.^{37,46–48} The spherical capsules, which were synthesized by a template method,^{80,81} contained a high carbon content (*i.e.*, >94 wt.%), exhibited a homogeneous morphology with diameter lower than 1 μm and a high contribution of pores with diameter lower than 8 nm, and could incorporate a large amount of ILs (70-85 wt.%). The discretization of the IL fluid into extremely small drops could drastically increase the gas/liquid contact area, thus enhancing the kinetics of adsorption

processes, while not affecting the solvent capacity of ILs.^{37,46–48} An example of SEM and TEM micrographs of empty hollow carbonaceous submicrocapsules is reported in Figure 6 together with micrographs of the same capsules filled with an IL (*i.e.*, 1-butyl-methylimidazolium acetate, [BMIM][acetate])⁴⁷. While this method is capable of synthesizing capsules with sub-micron diameters and narrow size distributions, it is the most involved method described so far, with several steps required to fabricate the low diameter shells, which are described in detail by Alonso-Morales *et al.*⁸¹ Despite the potential of this method, the range of suitable shell materials has not been explored extensively, as only capsules using activated carbon shells have been investigated so far.

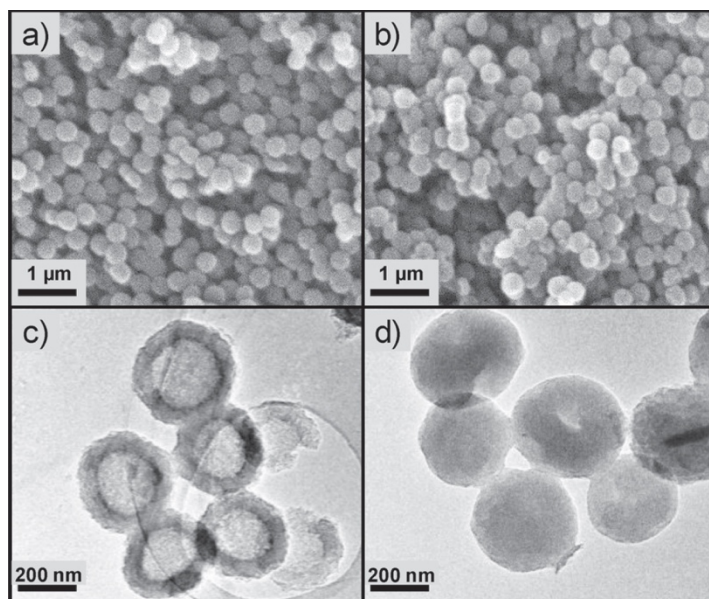


Figure 6. SEM (a) and TEM (c) micrographs of empty hollow carbonaceous submicrocapsules. SEM (b) and TEM (d) micrographs of hollow carbonaceous submicrocapsules containing 1-butyl-methylimidazolium acetate ([BMIM][OAc]). [Reprinted with permission from 47. Copyright (2019) American Chemical Society].

3. Areas of Application

In the following sections, the potential applications of encapsulated ILs in several fields are outlined. Considering the wide range of existing solutions that have been applied to exploit ILs in several technologies, among which it is critical to highlight supported ionic liquids (SILs) given

their potential use for the selective separation of chemical species^{23,27,82,83}, it is imperative to examine any advantages and shortcomings inherent to IL encapsulation as a IL discretization/immobilization method in comparison to more established methods. In general, the main advantages of encapsulated ILs over other IL-based technologies are: (a) greater surface area compared to solid supported ILs, which can increase mass transfer and catalysis rates⁸⁴, (b) facile modification and functionalization of the shell material, which opens the path towards greater customizability for specific applications^{85,86}, and (c) ease of integrating encapsulated IL in engineering systems, such as fixed or fluidized bed reactors and direct injection into fluid streams.

3.1. Carbon Capture

Emission of carbon dioxide (CO₂) in the atmosphere has for a long time been recognized to have negative environmental effects owing to its drastic effects leading to global warming.⁸⁷ In addition, the significant amount of CO₂ contained in natural gas, syngas, and biogas lowers the heating value of gases, while potentially causing corrosion of components and requiring additional energy for gas conversion.^{88,89} In the last decade, significant efforts have been spent in developing technologies for CO₂ capture and sequestration (CCS). Among them, the use of ILs in CCS has recently shown a rapid growth owing to the attractive properties of ILs together with their high affinity for CO₂.^{90–96} Despite the high CO₂ absorption capacity of ILs, a critical limitation in their use lies in their high viscosity, which can also increase upon CO₂ capture and limit mass transfer during the absorption process. As absorption rates have been recognized as a limiting factor in CO₂ capture systems that rely on ILs,^{97–99} extensive research has been performed in the development of solutions that consider both thermodynamic and kinetics aspects when selecting ILs. While supported IL phases (SILP), which rely on infusing an inorganic porous support with IL^{100,101} to increase the gas/liquid interfacial area, have been proposed as a way to increase the mass transport rate of CO₂ in IL, the limited capacity of SILP systems, due to low IL loading ratios of the porous media,^{102,103} is calling for further improvements.

The development of encapsulated ILs has emerged as an effective way to overcome these limitations by increasing the gas/liquid contact area and incorporating large amounts of IL in the capsules, thus making it attractive for CO₂ capture.^{37,46–48,57,78} As a particular example, Moya *et al.* encapsulated [BMIM][OAc] in hollow carbon microcapsules⁸¹ and provided evidence that the encapsulation did not affect the IL absorption capacity, but significantly enhanced the mass

transfer rate.⁴⁷ Additionally, the sorption capacity of the encapsulated ILs was shown to remain unchanged upon successive CO₂ sorption-desorption cycles. The authors also highlighted that when [BMIM][OAc] IL encapsulated in hollow carbon microcapsules is used in a fixed-bed reactor, the CO₂ sorption capacity per bed volume is comparable to that obtained for CO₂ carbonaceous absorbents reported in the literature.¹⁰⁴ These findings allowed the author to conclude that the large contact surface area of the IL capsules lead to fast and favorable CO₂ sorption even in fixed-bed operation. More recently, the same authors reported the encapsulation of an IL with an aprotic heterocyclic anion, namely trihexyl(tetradecyl)phosphonium 2-cyanopyrrolide ([P_{6,6,6,14}][2-CN₂Pyr]), in porous carbon microspheres.⁴⁶ ILs with aprotic heterocyclic anions are particularly promising for CCS owing to the ability of the anion to bond to CO₂ by reversible carboxylation with a N-heterocyclic carbene.^{105,106} The results reported by Moya *et al.* indicated an increase in the CO₂ absorption rates upon encapsulation compared to those of the neat IL, while maintaining the high absorption capacity characteristic of the IL.⁴⁶ Inspired by these results, the Pentzer group synthesized capsules using an IL-in-oil Pickering emulsion stabilized by alkylated graphene oxide nanosheets, which was coupled with the polymerization of hexamethylene diisocyanate and ethylene diamine. The encapsulated IL ([EMIM][TFSI]) was shown to reach full capacity, while unagitated bulk [EMIM][TFSI] could not reach the same thermodynamic equilibrium due to limitations in mass transfer.

3.2. Microreactors

The high viscosity and surface tension of ILs compared to conventional organic solvents, which result in unfavorable transport properties of these fluids, has constrained their use in additional applications, including biocatalysis^{107–109} and organic reactions^{110–112}. The discretization of ILs in microcapsules has been proposed as an effective method for overcoming this mass transport problem and opening the path for the exploitation of ILs as green solvents in catalysis. As a particular example, Weiss *et al.* reported the encapsulation of [BMIM][PF₆] within silica shells.³² The capsules were created by emulsifying [BMIM][PF₆] in water using surfactants, which was followed by interfacial polycondensation of tetraethoxysilane. The introduction of palladium acetate into [BMIM][PF₆] encapsulated within silica shells (Figure 7) allowed the authors to form Pd nanoparticles within the capsules. When used for the selective hydrogenation of alkynes, these catalytic capsules demonstrated up to 98% conversion of 1-octyne to octenes, compared to 77%

from a chemically identical formulation of Pd/SiO₂ catalyst with [BMIM][PF₆] as solvent. The capsules also showed negligible degradation in selectivity and conversion after three catalytic cycles. In this case, the confinement of Pd nanoparticles within the capsules was proposed to maintain a higher catalytic stability than more open solid supported catalysts, where particle aggregation during the reaction process reduces the catalytic surface area.

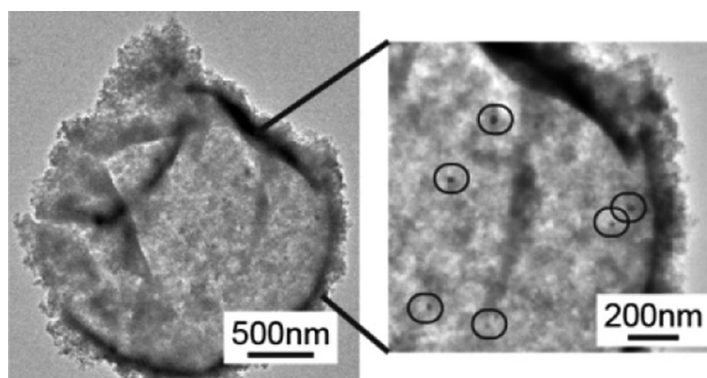


Figure 7. TEM micrographs of Pd/[BMIM][PF₆] in SiO₂, with black circles highlighting Pd nanoparticle formation within the capsules. [Reprinted with permission from 32. Copyright (2014) American Chemical Society].

The same authors later reported the encapsulation of [BMIM][PF₆] in polyurea shells by emulsification and interfacial polymerization.^{42,113} The dissolution of platinum acetylacetonate or cinchonine in the pre-emulsified IL enabled the authors to use the capsules as microreactors for hydrosilylation and Michael addition reactions. Due to capsule cracking during the first catalytic cycle,⁴² the authors subsequently encapsulated the same IL in polyurethane shells, which did not undergo any change in morphology during their use as microreactors for Michael addition reactions.¹¹³ Notably, a minimal decrease in activity (~5%) of the catalyst was also observed after three catalytic cycles, thus indicating the stability of the microreactor under operating conditions.

3.3. Waste Handling

IL have attracted considerable attention as potential fluids for removing different kinds of contaminants from mixtures.^{35,114–118} However, a significant challenge arises from the limited miscibility of IL in oil or water. One attractive solution to this problem lies in the encapsulation of

the ILs, which can be used as separation media, extractors, or as extraction media for active materials (*e.g.*, crown ethers)¹¹⁹, within polymer or composite shells. The resulting encapsulated ILs can be used in separation or extraction processes by mixing them with contaminated solutions followed by their isolation by filtration.^{31,35,120} The encapsulation of ILs has also the additional benefit of overcoming the mass transfer limitation due to the inherent high viscosity of ILs. Recently, Elizarova *et al.* developed a method for fabricating stable IL-in-water nano-emulsion via a low-energy phase reversal emulsification, which was followed by layer-by-layer polyelectrolyte deposition with the aim of increasing the stability of the emulsion.¹²⁰ The stabilized, multilayered IL nano-emulsion was shown to extract Cd²⁺ with nearly 100% efficiency and high selectivity. Notably, the encapsulated IL nano-emulsion exhibited long-term stability, as suggested by the lack of any statistically significant change in zeta-potential values after four months of storage. While other emulsion-based extraction systems have already been reported in the literature with similar extraction efficiency,^{121–123} the encapsulation process greatly increases the long-term stability and allows for the facile removal of the capsules from aqueous solutions compared to non-encapsulated emulsion droplets. More recently, Luo *et al.* prepared capsules of [BMIM][BF₄] using alkylated graphene oxide nanosheet surfactants in IL-in-oil emulsions followed by interfacial polymerization relying on the reaction between a diamine and diisocyanate.⁵² The encapsulated IL exhibited superior performance than bulk IL, as they could be used to remove ~98% of phenol from a contaminated oil (hexane) solution (Figure 8). This finding does not only demonstrate that the encapsulation of IL is a fully scalable method to prepare column-packing materials with high mass transport rates for the removal of phenol from oils, but also that this method can minimize formation of undesirable emulsions, a major limitation of liquid/liquid extraction processes.

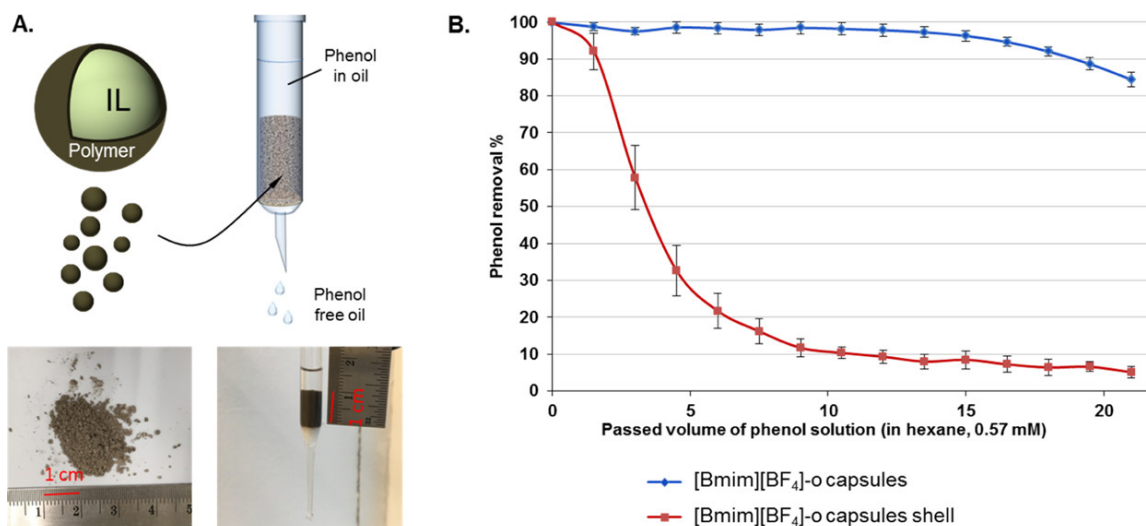


Figure 8. (a) Schematic of a column containing IL capsules that is employed for extracting phenol from hexane solutions. Photographs of the IL capsules and packed column are also displayed. (b) Phenol removal for the case of [BMIM][BF₄] capsules (blue trace) and the capsule shell (red trace, after IL extraction). [Reprinted with permission from 52. Copyright (2019) American Chemical Society].

3.4. Medical Materials

Several reviews, books, and book chapters have been dedicated to the biological properties of ILs^{124–127} as well as their pharmaceutical aspects.^{128–134} Furthermore, microencapsulation has been extensively explored a drug delivery method owing to high tissue specificity and therapeutic efficiency provided by surface functionalization and targeted release mechanisms.^{135,136} Despite this, the encapsulation of ILs for medical applications has been largely unexplored. One notable effort to exploit encapsulated ILs as agents susceptible to microwaves (MWs) and contrast agents to be used in magnetic resonance (MR) imaging for cancer MW thermotherapy was published in 2015 by Du *et al.*¹³⁷ The microcapsules, which were composed of [BMIM][BF₄] IL and iron oxide (Fe₃O₄) nanoparticles as the core and gelatin as the shell, exhibited strong MW absorbing property owing to the high susceptibility of IL to MW irradiation.^{128,138–140} Additionally, the presence of Fe₃O₄ nanoparticles in the capsules allowed monitoring the tumor response after the MW irradiation, thus enabling the effective assessment of the efficacy of the therapeutic treatment. The results reported by Du *et al.* thus clearly highlight the potential of using encapsulated IL for tumor therapeutics, while calling for further studies on the topic.

3.5. Energy storage

Supercapacitors have emerged as one of the most promising electrochemical storage devices¹⁴¹ owing to their high power density and good stability upon cycling. Supercapacitors can be classified into two main groups, namely electrochemical double-layer capacitors (EDLCs) that use porous carbon electrodes,^{141,142} and pseudocapacitors that employ metal oxides¹⁴³. In the case of the former, the charge is electrostatically stored at the electrode/electrolyte interface without, ideally, any faradaic reactions.¹⁴⁴ The high ionic conductivity, high thermal and chemical stability, together with the wide electrochemical window of ILs have made these fluids candidate electrolytes for EDLCs. However, the high viscosity of ILs together with their rather high surface tension can negatively affect the wetting behavior of IL electrolyte on the electrode. While several efforts have been spent in improving carbon electrodes by, for example, optimizing the pore size or changing their surface chemistry to enhance wettability,^{145,146} encapsulating ILs in shells made of reduced graphene oxide (rGO)/polyurea was recently proposed by Luo *et al.* as a method to increase the specific capacitance.⁵⁰ The rGO-IL capsules were used, together with functionalized cellulose binder, to create disk electrodes, which were subsequently covered by [BMIM][PF₆] and employed as both the anode and the cathode in a CR2032 coin cell containing a cellulose separator (which was also wet with [BIMIM][PF₆]). The specific capacitance at 18°C was higher across several scan rates (from 10 to 5000 mV s⁻¹) than the one measured using cells fabricated similarly, but having the anode and cathode made of either porous carbon (YP-50) or only the rGO material (Figure 9). The temperature dependence of the electrochemical performance of the coin cells provided the authors with insights into the impact of the architecture of anode/cathode on the performance: while the capacitance for the rGO-IL capsule cells at 60°C increases ~60% compared to its value at 18°C, the increase in capacitance at 60°C for the YP-50 cell was much more significant. This finding clearly demonstrated that the low ion mobility across [BMIM][PF₆] infused YP-50 due to high viscosity of ILs, especially at low temperature, strongly impacts the electrochemical performance, while highlighting the potential of rGO-IL capsules owing to their less dramatic change in capacitance with temperature.

Overall, the results presented by Luo *et al.* provided a clear demonstration of the potential use of ILs encapsulated within a shell made of rGO nanosheets in electrochemical double-layer capacitors. This work has paved the way towards the optimization of the nanoarchitecture to achieve higher specific capacitance values. In particular, research efforts

should be devoted to increase the interactions between IL and nanoshells (through, for example, the reduction of the capsule diameter) and decrease the amount of non-conductive polymer that is used to bind the rGO nanosheets, while increasing the amount of active electrode material (rGO).

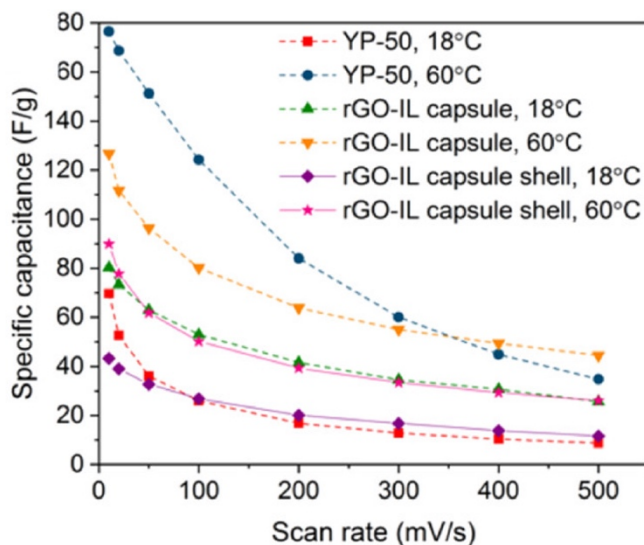


Figure 9. Specific capacitances for coin-cell supercapacitors made of anode/cathode material containing rGO-IL capsules, rGO-IL capsule shells, and YP-50 as a function of the cyclic voltammetry scan rate (red trace, after IL extraction). [Reprinted with permission from 50. Copyright (2019) American Chemical Society].

4. Conclusions and Outlook

In this paper we described the rationale for encapsulating ILs in organic or inorganic shells and summarized the different methods for discretizing ILs in microcapsules. The combination of the remarkable tunability of ILs originating from the high number of possible permutations of anions and cations with the possibility of tailoring the size, composition, and properties (*e.g.*, mechanical properties, permeability) of the shells is opening the path for the rational design of encapsulated ILs with task-specific properties for next-generation applications.

While this literature review highlighted the potential of encapsulating ILs in organic or inorganic capsules for several applications, significant work is required to shed light on the factors dictating the size, size distribution, and shape of the capsules for each specific methodology reported in published studies. Though it is generally understood that reducing capsule size increases total surface area, most encapsulation methods cannot produce capsules with radii less

than 5 μm (Table 1), restricting their use in several areas, such as biomedical applications. Morphologies beyond spherical core-shell structures, such as helical coils and multilayer structures, can be constructed with relative ease with microfluidic devices^{120,147–149}, but their performance compared to more conventional IL capsules in comparable tasks has not yet been thoroughly investigated. Finally, the physico-chemical and mechanical properties of the capsule shell should be more extensively evaluated using state-of-the-art characterization techniques. Gaining insights into the structure and composition of the material constituting the capsule shell could provide guidance for tailoring the encapsulation process to achieve specific shell properties (*e.g.*, permeability, stiffness) critical for the final implementation of encapsulated ILs in specific applications.

While published studies have mostly exploited the encapsulation of IL for overcoming kinetics limitations in mass transport, the discretization of IL in shells could also provide additional benefits, such as reducing undesirable IL chemical activity and mediating IL solubility. The prevalence of halogenated ions such as (trifluoromethylsulfonyl)imide (TFSI) and alkyl halides in most IL formulations frequently results in the formation of corrosive hydrogen halides when exposed to air due to the absorption of atmospheric water.^{150,151} The highly negative and undesirable effects when these ILs are employed in the presence of some engineering materials, including most steels, have called for the synthesis and evaluation of halogen-free ILs. However, these halogen-free ILs, such as those incorporating amino acids or chelated borates, tend to have limited solubility in fluids of importance for engineering applications, such as mineral or synthetic oils used for lubrication purposes^{152,153}. Following the successes demonstrated in utilizing encapsulated ILs in the lubrication of solid coatings^{43,55,154}, one ongoing research thrust in the laboratory of the authors is the encapsulation of oil-immiscible ILs to exploit them as friction- or wear-reducing agents in lubricants for engine oils.

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Notes

The authors declare no competing financial interests.

CRedit Authorship Contribution Statement

Jieming Yan: Conceptualization, Investigation, Writing - original draft, Writing - review & editing; **Filippo Mangolini:** Conceptualization, Investigation, Writing - original draft, Funding acquisition, Writing - review & editing; Funding acquisition.

Appendix

Table A.1. List of IL cations with the corresponding chemical structure used for encapsulation experiments.


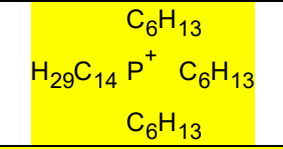
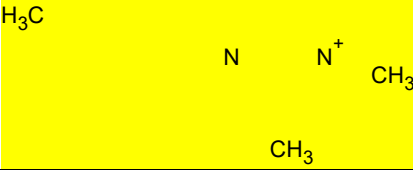

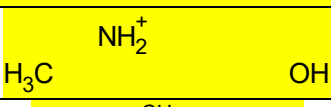
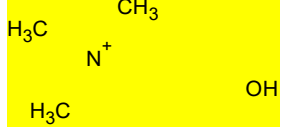
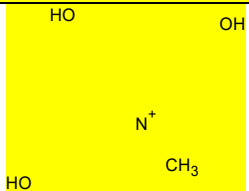
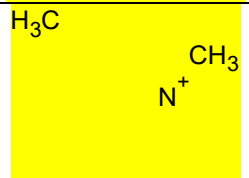
<i>Cation</i>	<i>Structure</i>
1-alkyl-3-methylimidazolium ([{n}MIM], {n} substitutes: E=ethyl, B=butyl, H=hexyl, O=octyl)	
Trihexyltetradecylphosphonium ([P _{6,6,6,14}])	
1-butyl-2,3-dimethylimidazolium ([BM ₂ IM])	
1-(2-hydroxyethyl)-3-methylimidazolium ([EtOH _{MIM}])	
N-methyl-2-hydro-xyethylammonium [N _{H2,Me,EtOH}][Pe]	
Choline	
tris(2-hydroxyethyl)methylammonium [(EtOH) ₃ MeN]	
1-methyl-1-propylpyrrolidinium [Mpp]	

Table A.2. List of IL cations with the corresponding chemical structure used for encapsulation experiments.

<i>Anion</i>	<i>Structure</i>
Bis(trifluoromethylsulfonyl)imide [TFSI] or [NTf ₂]	
Hexafluorophosphate [PF ₆]	
Tetrafluoroborate [BF ₄]	
Bis(2,4,4-trimethylpentyl)phosphinate [(C ₈) ₂ PO ₂]	
2-cyanopyrrolide [2-CN ₂ Pyr]	
Acetate [OAc]	
Pentanoate [Pe]	
Methyl sulfate [MeSO ₄]	
Dimethylphosphate (DMP)	

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