



Review article

Different roles of ionic liquids in lithium batteries

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HIGHLIGHTS

- All possible applications of ionic liquids in lithium batteries are reviewed.
- Potentials and limits of ILs for LIBs are described.
- Superior possibility of ionic liquid crystals as future electrolytes is presented.

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ABSTRACT

Ionic liquids are often named solvents of the future because of flexibility in design. This statement has given credence that ionic liquids should simply replace the problematic electrolytes of lithium batteries. As a result, the promising potentials of ionic liquids in electrochemical systems are somehow obscured by inappropriate expectations. We summarize recent advancements in this field, especially, ionic liquids as standalone electrolytes, additives, plasticizers in gel polymer electrolytes, and binders; and attempt to shed light on the future pathway of this area of research. Ionic liquids are not dilute media to serve as pure solvents in electrochemical systems where mobility of ions is the priority; instead, they can contribute to the ionic conductivity of various components in a battery system. Owing to the enormous possibilities of ionic liquids, it is not merely a matter of choice. Ionic liquids can be used to design novel types of electrolytes for a new generation of lithium batteries. A promising possibility, which is still at a very early stage, is *supercooled ionic liquid crystals* for fast ion diffusion through the guided channels of a liquid-like medium. This, of course, will be a breakthrough in the realm of electrochemistry, far beyond lithium battery field, when materialized.

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1. Introduction

The pioneering works of Humphry Davy for electrolysis of molten salts paved the path for electrochemistry in molten electrolytes [1], but the focus was practical for the preparation of reactive metals in elemental form. The next step was taken by Charles Martin Hall for the preparation of metallic aluminum *via* electrolysis of aluminum oxide dissolved in cryolite [2]. Due to the industrial importance of this method (which is still the primary approach for the production of aluminum), this idea was widely followed for industrial extraction of metals. The key feature of this idea was the possibility of forming eutectic molten salts to conduct

an electrolysis at lower temperatures.

Molten salts were subject to numerous studies from fundamental electrochemistry to various applications (metallurgy, fuel cells, *etc.*). Nevertheless, molten salts are usually the electroactive materials in electrochemical systems, exactly as it was in Davy's works. Ionic liquids (ILs) are indeed a game changer in electrochemistry by bringing new opportunities [3–9]. This is the main difference of molten salts and ILs; the former is the main point of interest in an electrochemical system, but the latter provides a new set of media for electrochemical reactions. Thus, ILs can find a universal place in the realm of electrochemistry.

From the chemistry point of view, ILs are ionic salts with large cations (usually organic) and anions (commonly both organic and inorganic), which make the ionic forces weaker, resulting in lower melting points. By definition (just common agreement indeed), ILs are molten salts with melting point less than 100 °C [10], and sometimes ILs with melting points lower than 25 °C are exclusively

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named room temperature ionic liquids (RTILs). This definition is subject to controversy due to the artificial threshold which does not have scientific significance. In the absence of any standard definition, the present one is commonly accepted, though, there are some misleading in the terminology of ILs.

The interface of molten salts and ionic liquids is chloroaluminate, *i.e.*, something in-between. Aluminum chloride has weak ionic bonds, and thus, a relatively low melting point (192 °C, if avoiding sublimation under pressure), but it has no noticeable ionic conductivity, as ions are not free to move in the corresponding molten medium. Eutectic mixtures of aluminum chloride with alkali metal chlorides have melting points as low as 70 °C [11,12]. The concept of eutectic molten salts is simple: introducing more ions to the system breaks the ordered structure of ionic solid resulting in a lower melting point. This also provides more freedom for ions to transport within the molten medium, and thus, improves the ionic conductivity [11,12]. In the best case, chloroaluminates are something between ionic and molecular liquids, and thus, they have been called quasi-molten salt [13]. Chloroaluminates have also been utilized as the first room temperature molten electrolytes of alkali metal batteries too [13–15], but they are not practical choices for commercialization. Another critical issue is instability of chloroaluminates in the presence of moisture.

In any case, the attractiveness of low-temperature molten salts paved the path for the development of ILs in which the ionic bonds are weak, and thus, the melting point is low; but not at the cost of losing ionic characteristics, contrary to chloroaluminates. It was common to emphasize non-chloroaluminates ILs in the literature, but in today's terminology, ILs are simply referred to the latter class. In other words, when claiming the unique roles of ILs in future technology, this is about organic ILs, not chloroaluminate ILs.

It should be emphasized that ILs have distinctive differences with molten salts, and it is not appropriate to categorize ILs as a subgroup of molten salts by simply setting the melting point.

- (i) Almost all ILs are capable of forming supercooled liquids below their melting points. This is indeed a common mistake in the literature; the liquidity of ILs should not be just judged by their melting points but the glass transition, as many ILs with melting point above room temperature are liquid at room temperature [16].
- (ii) Almost all ILs are subject to ionic pairing and subsequent self-aggregation due to large asymmetrical ions. In fact, the essential characteristic of ILs is not merely weak ionic bonds, but unusual charge distribution over ions, making the system much more complicated than molten ionic salts. This feature can be better understood in the transition from ionic liquids to (ionic) liquid crystals, in which long ions are indeed agglomerated in oriented directions.

The growing interest in ionic liquids is enormous, and various aspects of ionic liquids have been extensively reviewed [9,17–33].

For lithium batteries, which are the topic under consideration in this review, a common strategy is to test available ILs simply to replace problematic organic carbonates. It is impossible to find the best choices out of 10^{18} possible ILs [10] empirically. Nevertheless, only a few ionic liquids have been used for various applications in lithium batteries (Table 1). On the other hand, it is not wise to focus on adapting ILs to do the job of available organic carbonates, because of primary advantages such as inflammability. ILs have lots of additional capabilities to do better jobs. Apparently, this possibility comes at a price: ILs are too complicated (in comparison with

Table 1
Physical properties of common ILs for electrochemical systems. References in the last three columns point to representative papers (reference number) used the corresponding ILs for lithium battery applications as pure electrolytes, mixed with additives, or in gel polymer electrolytes, respectively.

Cation	Anion	T _m (K)	T _g (K)	Window (V)	σ _c (S m ⁻¹)	η (cp)	Pure	Mix	Gel
EMI	Cl	362.15 [377]		5 [378]	0.343–3.709 [379]		[380]		
	BF ₄	288.15 [379]	178 [381]	4.3 [382]	1.38 [383]	37.7 [382]	[59,80,204]		[232,383,383,384]
	TFSI	258.15 [385]	175.15 [385]	4.3 [386]	0.86 [387]	34 [388]	[74,76,93,104,150,151,387,389–394]	[157]	[395–398]
	BETI	272.15 [386]	188 [386]	4.1 [386]	0.34 [387]	61 [386]			[399]
	MSI	223.15 [385]		2.5 [385]	0.017 [389]	787 [385]			
	OTf	264 [388]		4.1 [388]	1.1 [387]				[400]
	TA	259 [388]		3.4 [388]	0.96 [390]	35 [388]			
	F(HF) _{2,3}			3.3 [401]	12 [402]	4.9 [403]			
	FSI						[63,78,126,402,404–407]		
	FSA						[73]		
	TFSA						[408]		
BMI	PF ₆							[409]	
	DCA	252.15 [410]	169.15 [410]						[411]
	BF ₄	190.65 [412]	188.15 [413]	6.1 [414]		219 [415]	[416]		[417]
	TFSI	269.15 [388]	169.15 [415]	4.76 [417]	0.39 [390]	52 [388]			[417]
	PF ₆	283.15 [415]	193.15 [415]	5 [414]	0.1 [418,419]	450 [415]			
C8MI	TA	233.15 [388]		5.7 [414]	0.32 [390]	73 [388]			
	TFSI		189.15 [420]	4.83 [417]		119.3 [417]			
	C10MI	244.15 [420]	190.15 [420]	4.89 [417]		152.8 [417]			
MDI	BF ₄			3.8 [421]					
	TA			5.7 [414]					
	TFSI			4.76 [417]					
	PF ₆			6.35 [417]					
M1,2E3I	TFSI			4.4 [388]		88 [388]			
	DMPI			5.2 [418]	0.3 [389]	60 [385]			
P13	Me			5.37 [422]	0.046 [423,424]				
	MSI	210.15 [425]		4.25 [425]					
	FSI						[63,78]		
P14	TFSI	285.15 [426]	183.15 [426]				[70,170,394,424,427,428]	[203,224,429]	[253,398]
	PF ₆							[409]	
	FSA						[73]		
	TFSI	255.15 [425]	186.15 [425]	6 [430]	0.22 [375]	85 [430]			
MSI			4 [425]		1680 [425]				

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