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Recent progresses on electrolytes of fluorosulfonimide anions for improving the performances of rechargeable Li and Li-ion battery

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ABSTRACT

Fluorosulfonimide anions, including bis(fluorosulfonyl)imide ($[(FSO_2)_2N]^-$, FSI^-) and (fluorosulfonyl)(perfluoroalkanesulfonyl)imide ($[(FSO_2)(n\text{–}C_mF_{2m+1}SO_2)N]^-$, $m = 1, 2, 4, 6, 8$, etc.) anions, play an increasingly important role in electrolyte materials for rechargeable Li and Li-ion battery. Recent advances in the synthesis of fluorosulfonimides and their alkali metal salts are summarized. The main advances on the electrolytes of these anions for improving the electrochemical performances of rechargeable Li and Li-ion battery are reviewed, in terms of the types of electrolytes, including conventional liquid carbonate electrolytes, ionic liquid electrolytes, molten salt electrolytes, and solid polymer electrolytes.

1. Introduction

Rechargeable Li-ion (i.e., graphitized carbon as anode) battery is widely used as power sources for portable electronics, because of its high energy and power density, and relatively long cycling life. It is also being intensively investigated for automotive and electricity storage applications. In today's commercial Li-ion battery, lithium hexafluorophosphate ($LiPF_6$) is being used as the dominating conducting salt. Solutions of $LiPF_6$ in dipolar aprotic organic carbonate solvents (mainly including ethyl carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC)) are being used as liquid nonaqueous electrolyte, which functions as Li-ion conductors between the anode and cathode electrodes [1]. This is mainly attributed to several key natures of $LiPF_6$-based electrolyte, among others, including high ionic conductivities and good electrochemical stability without aluminum (Al) current collector corrosion, good resistance toward oxidation and reduction, and excellent compatibility with both anode and cathode electrode materials [1]. More importantly, the success of $LiPF_6$ as conducting salt for Li-ion battery should thank for its unique compatibility with graphite anode, i.e., the formation of relatively stable solid electrolyte interphase (SEI) bestowed by the electrochemical reduction of $LiPF_6$–carbonate electrolytes on the surface of graphite anode with small irreversibility at the first cycle. The as-formed SEI film is a kinetically stable, ionically conductive, and electronically insulating film, which not only allows reversible intercalation of Li^+ ions in the graphite, but also protects both graphite electrode and organic electrolyte components from further detrimental reactions [1], thus allowing Li-ion battery to work with relatively long cycling life and desirable safety in room temperature region of −20 to 55 °C.

However, $LiPF_6$ is thermally instable and highly reactive toward protic impurities (e.g., water and alcohols) occurring in dipolar aprotic solvents. At elevated temperature, $LiPF_6$ in electrolyte can thermally decompose to produce strong Lewis acid, pentafluorophosphorane (PF_5) [2] through $LiPF_6\,(s) \rightarrow LiF\,(s) + PF_5\,(g)$, which in turn reacts with carbonate solvents to generate highly toxic substances (e.g., $(FCH_2CH_2)_2O$ [3]), or initiates an autocatalytic decomposition of electrolyte solutions [4], thus causing rapid capacity fading of Li-ion battery (i.e., short cycling life) [4,5], particularly at elevated temperatures. Furthermore, in dipolar aprotic solvents (e.g., carbonates), the "naked" PF_6^- anion is very reactive, and readily react with trace amounts of protic impurities (e.g., water and alcohols), which unavoidably occurs in the electrolyte solutions of $LiPF_6$ to produce HF [6]. It is well understood that low level of HF in the electrolytes can cause metal ion dissolution from cathode materials, and destroys solid electrolyte interphase (SEI) film formed on the carbon-based anodes [4(c),7], thus having a detrimental impact on the performance and safety of battery [4,5].

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Table 1
Abbreviations for some of representative fluorosulfonimide anions.

Anion	Name	Abbreviation
$[(FSO_2)_2N]^-$	Bis(fluorosulfonyl)imide	FSI^-
$[(FSO_2)(CF_3SO_2)N]^-$	(Fluorosulfonyl)(trifluoromethanesulfonyl)imide	$FTFSI^-$
$[(FSO_2)(C_2F_5SO_2)N]^-$	(Fluorosulfonyl)(pentafluoroethanesulfonyl)imide	$FPFSI^-$
$[(FSO_2)(n{-}C_4F_9SO_2)N]^-$	(Fluorosulfonyl)(perfluorobutanesulfonyl)imide	$FNFSI^-$

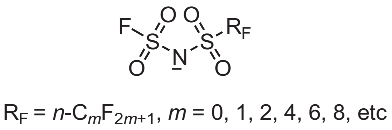


Fig. 1. Structures of bis(fluorosulfonyl)imide and (fluorosulfonyl)(perfluoroalkanesulfonyl)imide anions.

Therefore, advanced electrolyte materials, including new lithium salts and solvents, with improved properties are highly desired to overcome the drawbacks of conventional $LiPF_6$–carbonate electrolyte described above, thus improving cycling lifetime and safety of Li-ion battery. This is especially crucial for large-format battery, being developed for application in automotive industry, as problems in the cycling life and safety at elevated temperatures (>55 °C) are still the main barriers for extending the application of Li-ion battery using $LiPF_6$ into pure and hybrid electric vehicles.

Perfluorinated fluorosulfonyl imide anions (hereafter abbreviated as fluorosulfonimide, see Fig. 1 and Table 1) are a family of weakly coordinating anions, mainly including bis(fluorosulfonyl)imide ($[(FSO_2)_2N]^-$, FSI^-) and (fluorosulfonyl)(perfluoroalkanesulfonyl)imide ($[(FSO_2)(n{-}C_mF_{2m+1}SO_2)N]^-$, m = 1, 2, 4, 6, 8, etc.) anions, in which the nitrogen atom bonded directly to one or two inorganic fluorosulfonyl (FSO_2–) groups. In recent 10 years, they have been attracting an increasing attention in the arena of synthetic fluorine chemistry and Li and Li-ion battery, because their alkali metal salts and ionic liquids display many excellent and/or unique properties as electrolyte materials for improving the electrochemical performances of rechargeable Li (i.e., Li metal as anode) and Li-ion (i.e., graphitized carbon as anode) battery [8], which has not been seen with other anions. In the present review, we first give an overview of recent progresses on the preparation and properties of fluorosulfonimides, and their corresponding alkali metal salts and ionic liquids, and then concentrate on main advances in the application of these alkali metal salts and ionic liquids as electrolyte materials in Li and Li-ion battery. Some of the viewpoints or comments presented in the text are based on our accumulation and selves understanding in synthetic fluorine chemistry and electrolytes for Li and Li-ion battery, and the understanding on battery is mainly from the standpoint of electrolyte.

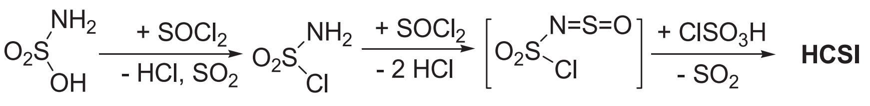
2. Preparation of fluorosulfonimide, and their alkali metal salts and ionic liquids

Some of earlier work on the preparation and reactivity of bis(fluorosulfonyl)imide (HFSI) and its precursor, bis(chlorosulfonyl)imide ($H[(ClSO_2)_2N]$, HCSI), has been well summarized in a review article published in 1997 [9]. Herein, we present recent advances in the preparation of fluorosulfonimide compounds in the order: (1) bis(chlorosulfonyl)imide ($H[(ClSO_2)_2N]$, HCSI), (2) bis(fluorosulfonyl)imide (HFSI), (3) ammonium salts of bis(fluorosulfonyl)imide, (4) alkali metal salts of bis(fluorosulfonyl)imide, (5) (fluorosulfonyl)(perfluoroalkanesulfonyl)imides and their alkali metal salts, and (6) ionic liquids of fluorosulfonimides.

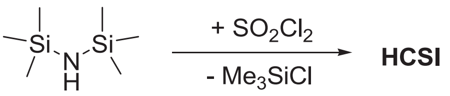
2.1. Bis(chlorosulfonyl)imide

Bis(chlorosulfonyl)imide ($H[(ClSO_2)_2N]$, HCSI) is a precursor for preparing HFSI. It is a highly moisture-sensitive, colorless, crystalline solid (melting point: 37 °C; boiling point: 115 °C/533 Pa) [10]. It is soluble and inert in a number of aprotic organic solvents at room temperature, such as benzene, nitrobenzene, and CH_3CN; however, it is reactive toward protic solvents (e.g., water or alcohols), and amine (NH_3) [10] and aliphatic amine [11], because of the high reactivity of the S–Cl bond in HCSI.

In 2005, Beran et al. [12] reported a new effective approach for the preparation of HCSI in nearly quantitative yield (reaction (1)), on the hypothesis that amidosulfuric acid (NH_2SO_3H) would react with thionyl chloride ($SOCl_2$) to generate the intermediate, $ClSO_2{-}N{=}S{=}O$, which further reacts with $ClSO_3H$ to yield HCSI. However, there are two major disadvantages for this reaction: (1) the reaction itself is not environmentally friendly, because of the generation of large amounts of acidic gases, SO_2 and HCl, as by-product; and (2) the efficiency of atom utilization (AU) of this reaction is low, as 53% of weight of starting materials are consumed for formation of the by-products, SO_2 and HCl.



(1)



(2)

HCSI was also effectively prepared by reaction of 1,1,1,3,3,3-hexamethyldisilazane (HMDS) with sulfuryl chloride (SO_2Cl_2) in CH_3CN (reaction (2)) [13]; however, this method is not appropriate for industrial preparation, because of the relatively high cost of HMDS.