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ARTICLE

Novel lithium and sodium salts of sulfonamides and bis(sulfonyl)imides: synthesis and electrical conductivity

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The preparation of new electrolytes for application in lithium or sodium batteries is described. Different salts of lithium and sodium sulfonamide and bis(sulfonyl)imide were prepared in good yields. Ionic conductivity measurements were performed on these salts and conductivities of 0.20 to 0.51 mS/cm, comparable to that of Li-TFSI, were obtained. The best conductivity was reached for the Li⁺ salt of a bis(sulfonyl)imide bearing a CF₃ and a 4-FC₆H₄ groups.

Introduction

Secondary lithium-ion batteries constitute today the most advanced energy storage technology, in ubiquitous use in various microelectronic and portable devices or in smart grids.¹⁻⁶ Furthermore, electric vehicles based on lithium batteries are in the final stage of industrial development. Concerns about a future limitation of the lithium reserves and an important price increase triggered research on secondary sodium batteries in recent years.^{7,8}

All these applications need electrolytes with excellent electrical conductivity, high safety and low cost.⁹ Currently, polymer gel electrolytes¹⁰ are mostly applied: they are made of a polymeric support (such as poly(vinylidene fluoride), PVdF) gelled with liquid organic solvents (typically organic carbonates) containing dissolved lithium salts, such as LiPF₆ or Li-bis(trifluoromethanesulfonyl)imide (Li-TFSI^{11,12}).

Advanced lithium and sodium battery electrolytes must satisfy many requirements,⁴ which make their development a very challenging task, including: (i) A large electrochemical stability window between oxidation at high anodic potentials and reduction at high cathodic potentials; (ii) Chemical stability with respect to the electrodes, including the ability to form rapidly a passivating solid-electrolyte-interface (SEI) layer, when the electrode potential lies outside the electrolyte stability window; (iii) Chemical stability at temperatures in the battery under high power; (iv) Li- or Na-ion conductivity σ (Li, Na) > 10⁻⁴ S/cm at the temperature of battery operation; (v) Very low electronic conductivity σ (e) < 10⁻¹⁰ S/cm; (vi) A transference number σ (Li, Na)/ σ total \approx 1, where σ total includes also partial conductivities by other ions in the electrolyte and by electrons; (vii) Retention of the electrode/electrolyte interface

during cycling; (viii) Safety, i.e. preferably non flammable and non explosive components; (ix) Low toxicity and low cost.

A major drawback of current lithium and sodium electrolytes is the fact that the transference number of the anion is generally higher than that of the cation; this leads to polarization phenomena at the electrodes, which are very detrimental to the battery cycling. Strategies to reduce the anion transference number include enhancing the anion molar mass in order to decrease its mobility or fixing the anion on a large macromolecule to impede its migration.^{9,13,14}

Few attempts at improving ionic conductivity have been realized via the salt approach, because the choice of anions suitable for lithium battery electrolytes is limited. Lithium bis(trifluoromethanesulfonyl)imide¹⁵ proved to be safe, thermally stable, and highly conducting and was even commercialized in the early 1990's. The application in lithium ion cells however never materialized, because Li-TFSI caused severe corrosion of Al current collectors. Efforts made to reduce the reactivity by structural modification of the imide anion extending the perfluorinated alkyl chain were found to be effective, but aromatic groups were not explored.⁹

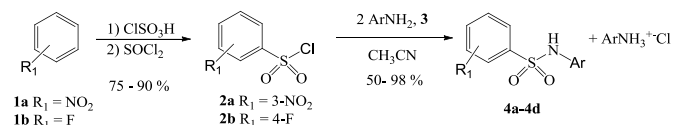
In this work, we present a new synthetic strategy for the preparation of lithium and sodium salts containing sulfonamide and bis(sulfonyl)imide anions, in particular with substituted phenyl groups. We also report their ionic conductivity, determined by impedance spectroscopy. The high ionization degree of superacidic bis(sulfonyl)imides,¹² together with the high anion mass and the excellent redox stability of the aromatic groups are promising properties for battery electrolyte applications.

Results and discussion

Preparation of Li⁺ and Na⁺ salts of sulfonamides and bis(sulfonyl)imides

With the aim to evaluate the effect of several functional groups and to establish structure-property relationships in the field of electrical conductivity, a series of differently substituted lithium and sodium sulfonamide and bis(sulfonyl)imide salts were prepared in anhydrous form. The different salts were synthesized according to two different procedures.

For lithium and sodium sulfonamides, the starting materials are the aromatic compounds **1a** and **2b**, bearing electron-withdrawing substituents, such as nitro or fluorine groups, respectively. A chlorosulfonation reaction was carried out, adapting the reported literature procedures.^{16,17} The chlorosulfonation, as presented in Scheme 1, proceeded through the reaction of **1a-1b** with chlorosulfonic acid, followed by treatment with sulfonyl chloride. The derivatives **2a**, **2b**, with the chlorosulfonyl group at the 3- or 4-position, respectively, were obtained in almost quantitative yields after purification by column chromatography. These compounds could be prepared at a 10 g-scale.

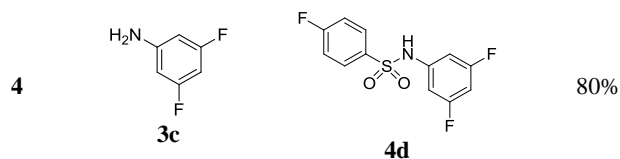


Scheme 1 Preparation of sulfonamides **4**

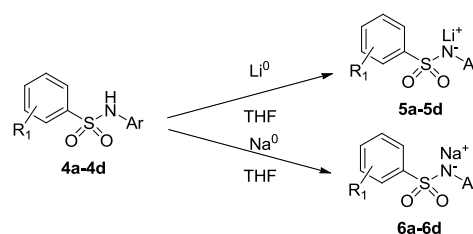
The reaction of **2** with different aromatic amines **3**, led to the formation of sulfonamides **4a-4d**. The reactions were carried out in acetonitrile, with two equivalents of amine, in order to trap the evolving HCl. Ammonium chloride being insoluble in the medium, the sulfonamides could be purified by filtration. Good yields for compounds **4** were generally obtained, as presented in Table 1.

Table 1 Preparation of sulfonamide **4**

Entry	Amines 3	Sulfonamides 4	Yield of 4
1			98%
2			96%
3			50%



The preparation of lithium salts of sulfonamides is described in the literature by the use of LiOH.^{18,19} However, this procedure does not allow getting the desired sulfonamides as anhydrous salts. We prepared the corresponding lithium salts by the direct reaction of **4** with lithium metal in THF. The procedure afforded the Li⁺ derivatives **5a-5d** in quantitative yields, as illustrated in Scheme 2 and in Table 2.



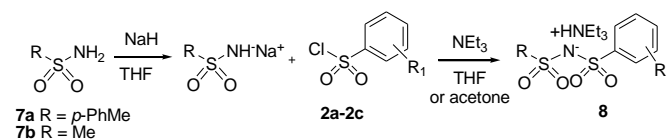
Scheme 2 Synthesis of Li⁺ and Na⁺ sulfonamide salts **5** and **6**

By reaction of sulfonamides **4** with sodium metal in THF, the corresponding Na⁺ salts, **6**, could be obtained in anhydrous form and in quantitative yields (Scheme 2, Table 2).

Table 2 Synthesis of Li⁺ and Na⁺ sulfonamide salts **5** and **6**

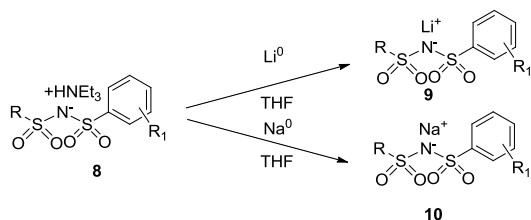
Entry	Sulfonamides	Sulfonamide salts	Yield
1	4a	5a	>98%
2	4a	6a	98%
3	4b	5b	97%
4	4b	6b	>98%
5	4c	5c	98%
6	4c	6c	98%
7	4d	5d	>98%
8	4d	6d	97%

For bis(sulfonyl)imide salts, the preparation involved the reaction of aryl chlorosulfonyl derivatives **2** with several deprotonated sulfonamides **7** (Scheme 3). The coupling was carried out in THF under a room temperature basic medium, either with NaH or with triethylamine. The coupling reaction could also be carried out in acetone at room temperature using triethylamine.

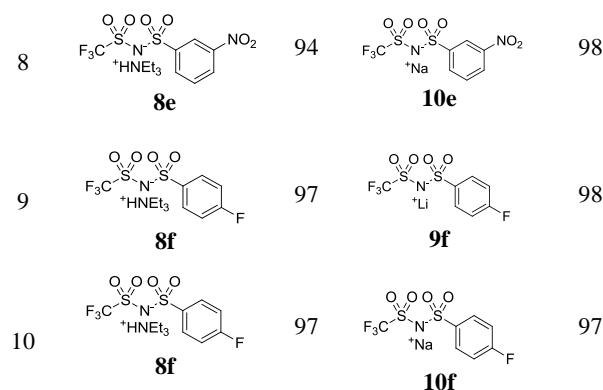


Scheme 3 Synthesis of ammonium bis(sulfonyl)imide salts **8**

Triethylamine was used as the tertiary amine in order to obtain a series of ammonium salts **8a-8f**, which were purified by trituration in diethyl ether. The yields of **8** are given in Table 3. The Li⁺ salts of the corresponding bis(sulfonyl)imides, **9**, were obtained by treatment of salts **8** with lithium metal in THF. Following the same procedure with sodium metal, the bis(sulfonyl)imide Na⁺ salts, **10**, were obtained in quantitative yields (Scheme 4, Table 3).

Scheme 4 Synthesis of Li⁺ and Na⁺ bis(sulfonyl)imide salts **9** and **10**Table 3. Synthesis of Li⁺ and Na⁺ bis(sulfonyl)imide salts **9** and **10**.

Entry	Ammonium salts 8	Yield of 8 (%)	Li ⁺ /Na ⁺ salts 9, 10	Yield of 9, 10 (%)
1		51		98
2		51		99
3		55		97
4		55		98
5		63		97
6		59		96
7		94		97

Ionic conductivity of the Li⁺ and Na⁺ salts of sulfonamides and bis(sulfonyl)imides

The concentration dependence of the ionic conductivity is shown for the sodium salt **6a** between 0.01 and 0.1 mol/L as illustrated in Figure 1.

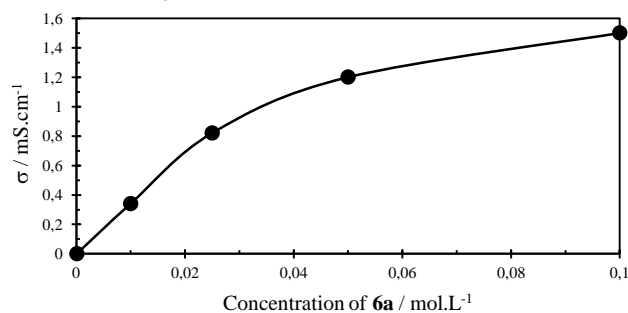


Figure 1. Concentration dependence of the ionic conductivity of solutions of salt **6a** in DMSO at 25 °C.

A linear relation between conductivity and concentration, expected for completely dissociated strong electrolytes, was observed at very low concentrations. At higher concentration, the increase of conductivity flattens out, because the ionic mobility decreases at large salt concentrations due to the increased inter-ionic interactions and to a higher solution viscosity.⁹ This classical behavior is well documented in the framework of the Debye-Hückel theory.²³ The conductivity observed at a concentration of 0.1 mol/L (1.5 mS/cm) can be compared with data reported in the literature at higher concentration (5.1 mS/cm in 1.0 mol/L solution in propylenecarbonate (PC),⁹ 4-7 mS/cm in mixtures with ionic liquids²⁴).

0.01 mol/L solutions of Li⁺ and Na⁺-salts **5**, **6**, **9** and **10** were prepared in a glove box using dimethylsulfoxide (DMSO) as the solvent. The solutions were analyzed using a closed 1 cm³ conductivity cell with 1 cm² platinum electrode area at 25 °C. An impedance spectrometer EG&G model 6310 was used; the amplitude of the ac signal was typically 20 mV at frequencies between 100 kHz and 1 Hz.

Figure 2 shows the conductivity of 0.01 molar solutions of the various Li⁺ and Na⁺ salts in DMSO, a high dielectric constant

solvent. The conductivity of Li-TFSI, which is considered here as a reference, is consistent with literature data (0.32 mS/cm in 0.01 mol/L solution in PC/ethylmethylcarbonate mixtures,^{20,21}

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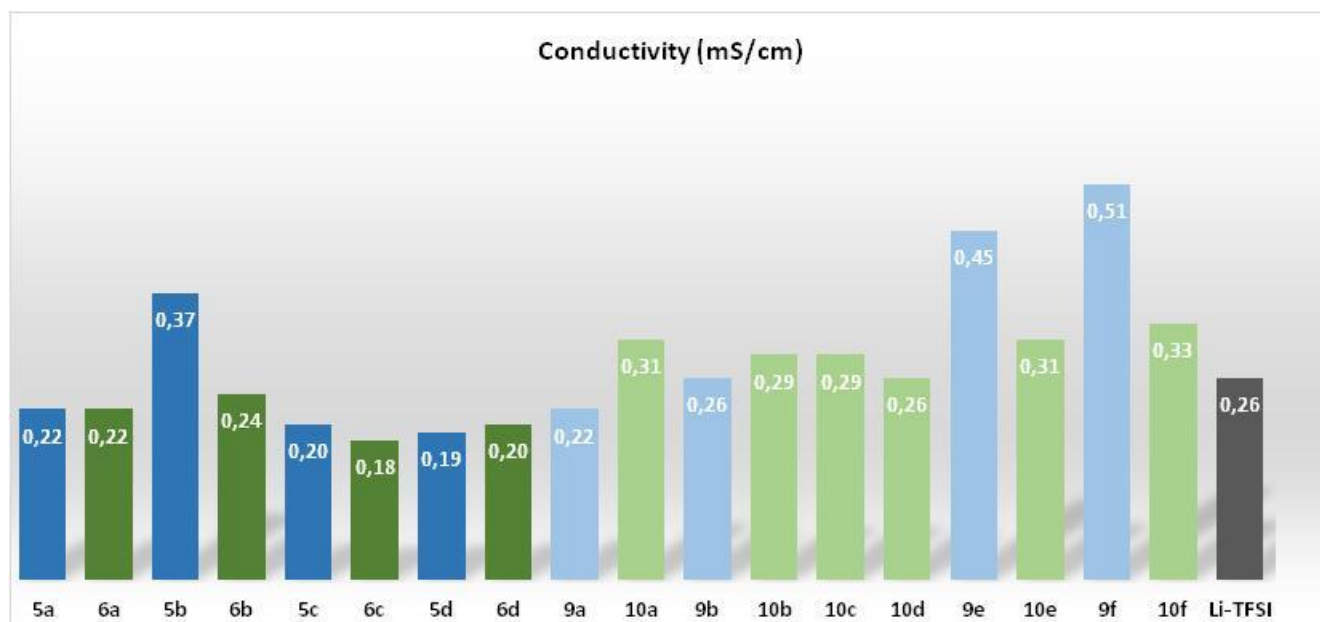


Figure 2. Ionic conductivity of Li^+ and Na^+ sulfonamide (**5**, **6**) and bis(sulfonyl)imide (**9**, **10**) salts in 0.01 mol/L solution in DMSO at 25 °C.

2.1 mS/cm in 1 mol/L solution in DMSO²²). The good ion conductivity is supposed to be the result of a compromise between a high degree of dissociation and a low ionic mobility.⁹ The conductivity values of the new Li^+ and Na^+ salts are in the order of 0.2 to 0.5 mS/cm; the conductivity values are very competitive with Li-TFSI and, although quite similar, some observations on substituent effects can be made. The average conductivity of the sulfonamides (**5**, **6**) is slightly lower than that of the bis(sulfonyl)imides (**9**, **10**). This fact can be related to a slightly lower dissociation degree of the sulfonamides.

The conductivity of salts with a fluorine group at the *para*-position on the aromatic ring is superior to that with a nitro substituent at the *meta*-position.

The high conductivity of the bis(sulfonyl)imides with a trifluoromethyl moiety directly attached to a sulfonyl group (**9e**, **10e** and **9f**, **10f**) is consistent with the high electron-withdrawing effect of the CF_3 moiety involving an increase of the ionization degree. Two of these salts, namely **9e** and **9f**, offered a higher conductivity than the reference compound Li-TFSI. These Li^+ salts could therefore be candidates for the replacement of Li-TFSI in Li-batteries. The highest conductivity was measured for salt **9f**, which presents a directly linked trifluoromethyl moiety and a fluorine atom instead of a nitro group on the aromatic ring.

The conductivity of the Na^+ salts was generally lower than that measured for the corresponding Li^+ salts. This is probably related to the smaller size of the Li^+ ion and its higher mobility.

Conclusions

New lithium and sodium salts of sulfonamide and bis(sulfonyl)imide were prepared and ionic conductivity measurements were realized. The results obtained are comparable or even superior to TFSI-Li, a salt generally used as electrolyte (0.26 ms/cm). The best result was obtained with *N*-(trifluoromethanesulfonyl)-*p*-fluorobenzenesulfonamide lithium salt, **9f**, presenting an ionic conductivity of 0.51 ms/cm. The conductivities with sulfonamide salts were lower as compared to those observed for the salts derived from bis(sulfonyl)imides. Finally, the obtained ionic conductivities for the lithium salts were generally superior to those measured for the corresponding sodium salts. This fact is most probably due to the higher mobility and the lower size of the Li^+ ions as compared to the Na^+ ions.

Experimental†

Details on the analysis of the different compounds are given in the ESI.

- Preparation of benzenesulfonyl chlorides **2a-2b**.

In a two-necked 25 mL flask fitted with a condenser, the aromatic compound **1** (nitrobenzene or fluorobenzene) (81 mmol) was added, followed by addition of chlorosulfonic acid (106 mmol) *via* a syringe. The mixture was heated at 150 °C for 2 h 30. The solution was cooled to room temperature and thionyl chloride was added (1.42 equiv.) and the mixture was then heated at 150 °C for 3 h. The solution was cooled to room temperature and quenched with 20 mL of water. The aqueous phase was extracted with 3 × 20 mL of ethyl acetate. The combined organic phases were dried with MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by chromatography on silica gel using a mixture of dichloromethane / cyclohexane (50/50) as the eluent.

- Preparation of sulfonamides **4a-4d**.

In a 50 mL flask, the sulfonyl chloride **2** (2.3 mmol), and the amine **3** (4.8 mmol) were added to 20 mL acetonitrile. The solution was stirred at room temperature for 2 h, the mixture was filtered off and the filtrate was evaporated. The residue was purified by trituration in diethyl ether (3 × 20 mL) and dried under vacuum overnight.

- Preparation of Li⁺ et Na⁺ sulfonamide salts **5a-5d** and **6a-6d**.

In a 25 mL flask under nitrogen, the sulfonamide **4** (1 mmol) was dissolved in 15 mL of THF. Lithium or sodium metal (1.1 mmol) was added to the solution and after 18 h at room temperature the mixture was filtered off. The residue obtained was triturated with 2 × 10 mL of acetonitrile and then dried under vacuum overnight.

- Preparation of Li⁺ and Na⁺ bis(sulfonyl)imide salts **9a-9b**, **9e-9f** and **10a-10f**.

In a 50 mL flask are introduced 20 mL of acetone, then added NaH (2.8 mmol) and triethylamine (2.8 mmol) and the sulfonamide **7** (2 mmol). After stirring for 15 min at room temperature the sulfonyl chloride **2** (2 mmol) was added. After stirring for 3 h at room temperature, the precipitate formed was filtered off and the filtrate was concentrated. The oil was triturated with 2 × 20 mL of Et₂O. After filtration, the solid was dissolved in 20 mL of CH₂Cl₂ and the solution was filtered. The solid obtained corresponds to the sodium salt, while the filtrate contained the ammonium salt of triethylamine **8**. The two solids were dried under vacuum. The preparation of **9e-9f** and **10e-10f** was realized with 5.6 mmol of triethylamine without deprotonation with NaH. After 3 days stirring at room temperature and the same workup as previously the ammonium salt **8** was obtained.

Then in a 25 mL flask under nitrogen, the ammonium of bis(sulfonyl)imide **8** (1 mmol) were dissolved in 15 mL of THF. Sodium or lithium metal (1.1 mmol) was added to the solution and after 18 h at room temperature the mixture was filtered off. The solid phase was triturated with 2 × 10 mL of acetonitrile and then dried under vacuum.

- Conductivity measurements.

An impedance spectrometer EG&G model 6310 was used; the amplitude of the ac signal was typically 20 mV at frequencies between 100 kHz and 1 Hz.

Solutions (0.01 mol/L) of Li⁺ and Na⁺-salts **5**, **6**, **9** and **10** were prepared in a glove box using dimethylsulfoxide (DMSO) as

the solvent. The solutions were analyzed using a closed 1 cm³ conductivity cell with 1 cm² platinum electrode area at 25 °C.

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Notes and references

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† Electronic Supplementary Information (ESI) available: procedure and analysis for the preparation of compounds **2a-2b**, **4a-4d**, **5a-5d**, **6a-6d**, **9a-9b**, **9e-9f** and **10a-10f**. See DOI:

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