NJC

PAPER

View Article Online
View Journal | View Issue

Cite this: *New J. Chem.*, 2014, **38**, 6193

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

Vincent Morizur,[a] Sandra Olivero,[a] Jean Roger Desmurs,[b] Philippe Knauth[c] and Elisabet Duñach*[a]

Received (in Montpellier, France) 17th July 2014, Accepted 23rd September 2014

DOI: 10.1039/c4nj01191k

www.rsc.org/njc

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^{-1}, comparable to those of Li-TFSI, were obtained. The best conductivity was reached for the Li$^+$ salt of a bis(sulfonyl)imide bearing CF_3 and 4-FC_6H_4 groups.

Introduction

Secondary lithium-ion batteries constitute today the most advanced energy storage technology, ubiquitously used 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 electrolytes[10] 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 $LiPF_6$ 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^{-1} at the temperature of battery operation; (v) very low electronic conductivity σ (e) $<$ 10^{-10} S cm^{-1}; (vi) a transference number σ (Li, Na)/σ total $\approx$ 1, where σ total includes also partial conductivities by other ions in the electrolyte; (vii) retention of the electrode/electrolyte interface during cycling; (viii) safety, *i.e.* preferably non-flammable and non-explosive components; and (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 the ionic conductivity have been realized *via* the salt approach, because the choice of anions suitable for lithium battery electrolytes is limited. Lithium bis(trifluoromethanesulfonyl)imide[15] proved to be safe, thermally stable, and highly conducting and was even commercialized in the early 1990s. The application of lithium ion cells, however, never materialized because the 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

---

[a] *Institut de Chimie de Nice, Université de Nice-Sophia Antipolis, CNRS, UMR 7272, Faculté des Sciences, Parc Valrose, 06108 Nice cedex 2, France. E-mail: dunach@unice.fr*

[b] *CDP Innovation, G2C Business Center, 63 Rue André Bollier, 69307 Lyon, France*

[c] *Aix Marseille Université, CNRS, Madirel (UMR 7246), 13397, Marseille Cedex 20, France*

† 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: 10.1039/c4nj01191k

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 of evaluating the effect of several functional groups and establishing 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.

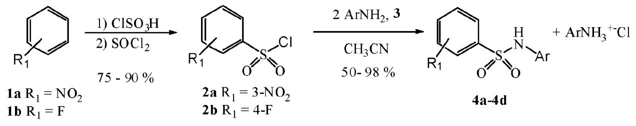
For lithium and sodium sulfonamides, the starting materials are the aromatic compounds **1a** and **2b**, bearing electron-withdrawing substituents, such as nitro or fluorine groups, respectively. A chlorosulfonation reaction was carried out, adapting the reported literature procedures.[16,17] The chlorosulfonation, 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.

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.

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.

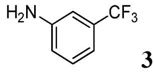
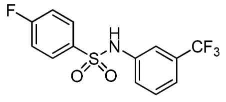
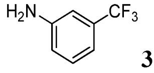
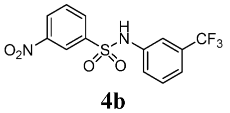
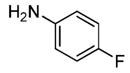
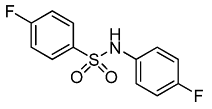
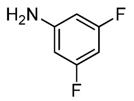
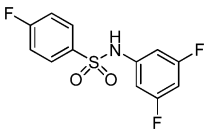
By the reaction of sulfonamides **4** with sodium metal in THF, the corresponding Na^+ salts, **6**, could be obtained in anhydrous form and in quantitative yields (Scheme 2 and Table 2).

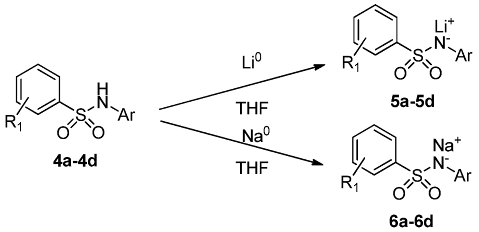
For bis(sulfonyl)imide salts, the preparation involved the reaction of aryl chlorosulfonyl derivatives **2** with several deprotonated sulfonamides **7** (Scheme 3). The coupling was carried out in THF under a room temperature basic medium, either with NaH or with triethylamine. The coupling reaction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



Scheme 1 Preparation of sulfonamides **4**.

Table 1 Preparation of sulfonamides **4**

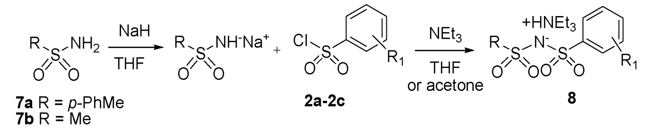
Entry	Amines **3**	Sulfonamides **4**	Yield of **4** (%)
1	 **3a**	 **4a**	98
2	 **3a**	 **4b**	96
3	 **3b**	 **4c**	50
4	 **3c**	 **4d**	80



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

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

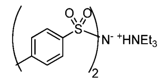
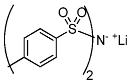
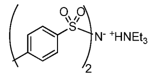
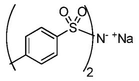
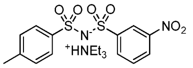
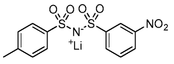
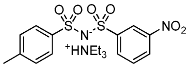
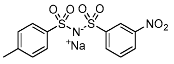
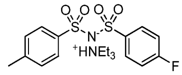
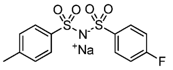
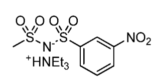
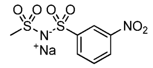
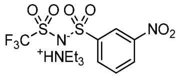
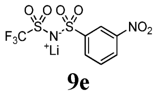
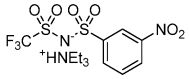
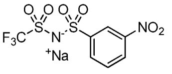
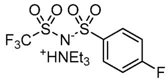
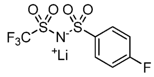
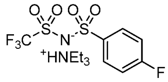
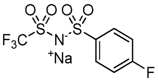
Entry	Sulfonamides	Sulfonamide salts	Yield (%)
1	**4a**	**5a**	>98
2	**4a**	**6a**	98
3	**4b**	**5b**	97
4	**4b**	**6b**	>98
5	**4c**	**5c**	98
6	**4c**	**6c**	98
7	**4d**	**5d**	>98
8	**4d**	**6d**	97



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

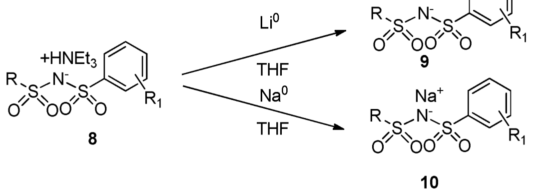
Table 3 Synthesis of Li^+ and Na^+ bis(sulfonyl)imide salts **9** and **10**

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

bis(sulfonyl)imide Na^+ salts, **10**, were obtained in quantitative yields (Scheme 4 and Table 3).

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

The concentration dependence of the ionic conductivity for the sodium salt **6a** between 0.01 and 0.1 mol L^{-1} is illustrated in Fig. 1.



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

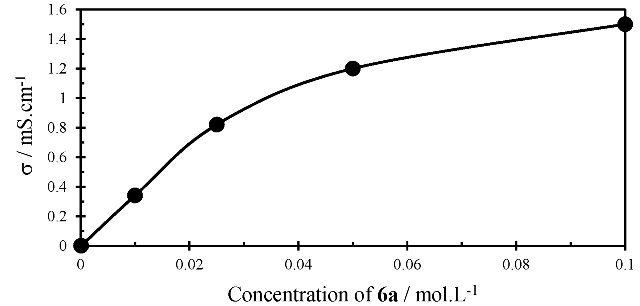


Fig. 1 Concentration dependence of the ionic conductivity of solutions of salt **6a** in DMSO at 25 °C.

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} (1.5 mS cm^{-1}) can be compared with data reported in the literature at higher concentration (5.1 mS cm^{-1} in 1.0 mol L^{-1} solution in propylenecarbonate (PC),[9] 4–7 mS cm^{-1} in mixtures with ionic liquids[24]).

0.01 mol L^{-1} 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 cm^3 conductivity cell with a 1 cm^2 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.

Fig. 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^{-1} in 0.01 mol L^{-1} solution in PC–ethylmethylcarbonate mixtures,[20,21] 2.1 mS cm^{-1} in 1 mol L^{-1} solution in DMSO[22]). The good ionic 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^{-1}; 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 involved and an increase in the ionization degree. Two of these salts, namely **9e** and **9f**, offered a higher conductivity than the reference compound

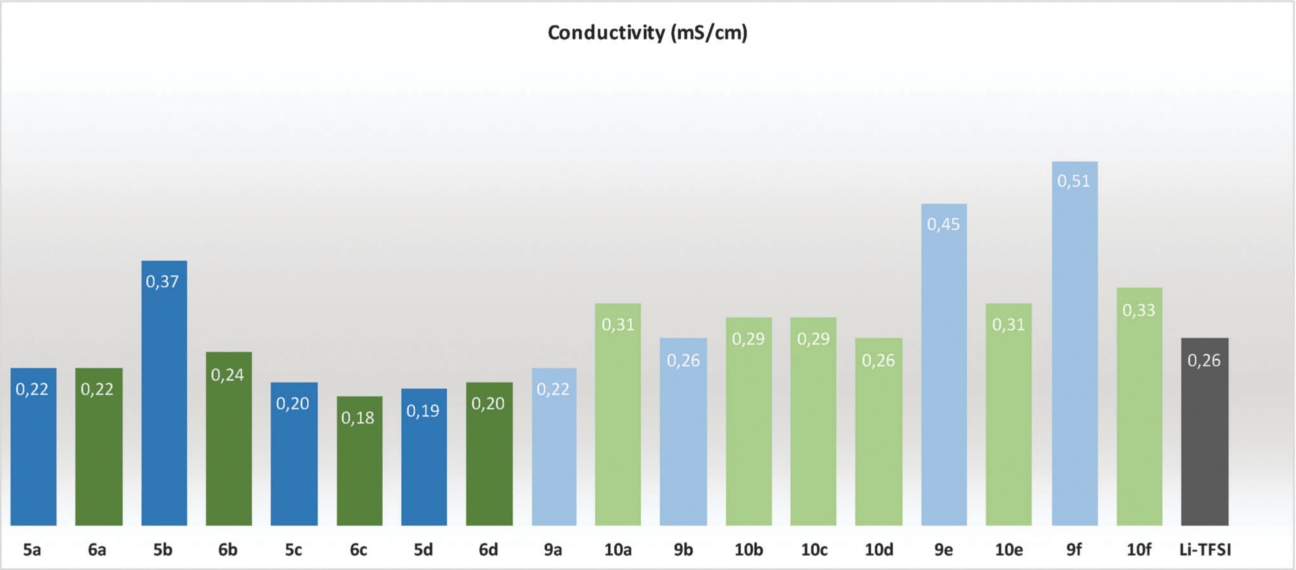


Fig. 2 Ionic conductivity of Li^+ and Na^+ sulfonamide (**5**, **6**) and bis(sulfonyl)imide (**9**, **10**) salts in 0.01 mol L^{-1} solution in DMSO at 25 °C.

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 an electrolyte (0.26 mS cm^{-1}). The best result was obtained with *N*-(trifluoromethanesulfonyl)-*p*-fluorobenzenesulfonamide lithium salt, **9f**, presenting an ionic conductivity of 0.51 mS cm^{-1}. 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 (ESI†)

Details of 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 min. 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 $MgSO_4$, 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^+ and 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, NaH (2.8 mmol), 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 Et_2O. After filtration, the solid was dissolved in 20 mL of CH_2Cl_2 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 of stirring at room temperature and following the same procedure as that used previously the ammonium salt **8** was obtained.

Then in a 25 mL flask under nitrogen, the ammonium of bis(sulfonyl)imide **8** (1 mmol) was 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^{-1}) 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 cm^3 conductivity cell with a 1 cm^2 platinum electrode area at 25 °C.

Acknowledgements

We thank the Région PACA for a fellowship for V.M.

Notes and references

1 J. M. Tarascon and M. Armand, *Nature*, 2001, **414**, 359–367.
2 B. Dunn, H. Kamath and J.-M. Tarascon, *Science*, 2011, **334**, 928–935.
3 Z. Yang, J. Zhang, M. C. W. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon and J. Liu, *Chem. Rev.*, 2011, **111**, 3577–3613.
4 J. B. Goodenough and Y. Kim, *Chem. Mater.*, 2010, **22**, 587–603.
5 M. R. Palacin, *Chem. Soc. Rev.*, 2009, **38**, 2565–2575.
6 M. Armand and J. M. Tarascon, *Nature*, 2008, **451**, 652–657.
7 K. B. Hueso, M. Armand and T. Rojo, *Energy Environ. Sci.*, 2013, **6**, 734–749.
8 M. D. Slater, D. Kim, E. Lee, M. Doeff and C. S. Johnson, *Adv. Funct. Mater.*, 2013, **23**, 947–958.
9 K. Xu, *Chem. Rev.*, 2004, **104**, 4303–4418.
10 J. W. Fergus, *J. Power Sources*, 2010, **195**, 4554–4569.
11 H. Sakaebe and H. Matsumoto, *Electrochem. Commun.*, 2003, **5**, 594–598.
12 K. Hayamizu, Y. Aihara, S. Arai and C. G. Martinez, *J. Phys. Chem. B*, 1999, **103**, 519–524.
13 R. Meziane, J. P. Bonnet, M. Courty, K. Djellab and M. Armand, *Electrochim. Acta*, 2011, **57**, 14–19.
14 R. Bouchet, S. Maria, R. Meziane, A. Aboulaich, L. Lienafa, J.-P. Bonnet, T. N. T. Phan, D. Bertin, D. Gigmes, D. Devaux, R. Denoyel and M. Armand, *Nat. Mater.*, 2013, **12**, 452–457.
15 J. Foropoulos, Jr. and D. D. DesMarteau, *Inorg. Chem.*, 1984, **23**, 3720–3723.
16 X. de Leval, M. Ilies, A. Casini, J.-M. Dogne, A. Scozzafava, E. Masini, F. Mincione, M. Starnotti and C. T. Supuran, *J. Med. Chem.*, 2004, **47**, 2796–2804.
17 A. Chakrabarti, R. Filler and B. K. Mandal, *Solid State Ionics*, 2010, **180**, 1640–1645.
18 M. B. Herath, S. E. Creager, R. V. Rajagopal, O. E. Geiculescu and D. D. DesMarteau, *Electrochim. Acta*, 2009, **54**, 5877–5883.
19 S. Lee, D. Jamieson and P. L. Fuchs, *Org. Lett.*, 2009, **11**, 5–8.
20 T. Umecky, Y. Saito, Y. Okumura, S. Maeda and T. Sakai, *J. Phys. Chem. B*, 2008, **112**, 3357–3364.
21 M. Ue and S. Mori, *J. Electrochem. Soc.*, 1995, **142**, 2577–2581.
22 D. Xu, Z. L. Wang, J. J. Xu, L. L. Zhang, L. M. Wang and X. B. Zhang, *Chem. Commun.*, 2012, **48**, 11674–11676.
23 G. Kortüm, *Treatise on Electrochemistry*, Elsevier, Amsterdam, New York, 2nd edn, 1965.
24 D. Monti, E. Jonsson, M. R. Palacin and P. Johansson, *J. Power Sources*, 2014, **245**, 630–636.