

Corrosion of aluminum at high voltages in non-aqueous electrolytes containing perfluoroalkylsulfonyl imides; new lithium salts for lithium-ion cells

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Abstract

New lithium bis-perfluoroalkylsulfonyl imide salts were recently synthesized in our laboratories whose properties make them promising candidates for lithium-ion batteries. The salts have good conductivity, cycling characteristics and excellent thermal and hydrolytic stability. In the focus of this paper are the corrosion properties of the aluminum current collector in electrolytes based on these salts. High protection potentials at aluminum in bisperfluoroethylsulfonyl imide electrolytes were observed. Based on the surface analysis of the protective film, a correlation of the molecular weight of the anions to their protective properties was established. © 1997 Elsevier Science S.A.

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1. Introduction

Lithium hexafluorophosphate (LiPF_6) is by far the most commonly used conducting lithium salt in secondary lithium-ion batteries. Electrolytes containing LiPF_6 usually show good conductivity, good electrochemical stability and do not promote aluminum corrosion, a material commonly used as a positive electrode current collectors. LiPF_6 , however, suffers from both thermal and hydrolytic instability reacting with water to yield HF and thermally decomposing to LiF and PF_5 [1]. The thermal stability can be negatively affected by the presence of small amounts of water [1]. Since it is practically impossible to remove all traces of water from commercial lithium-ion cells, some level of HF formation can be expected. Acidic conditions have been suggested as being detrimental to the cycling performance of $\text{Li}_2\text{Mn}_2\text{O}_4$ [2].

Several years ago a promising new salt, lithium bistrifluoromethylsulfonyl imide (LiTFSI), with much greater thermal and hydrolytic stability appeared [3,4]. The practical use of this salt in liquid electrolytes never materialized due to severe corrosion of aluminum current collectors. Recently, several new perfluoroalkylsulfonyl imides lithium salts were synthesized in our laboratories. In this paper we report some of the properties of these new salts with emphasis on the aluminum

corrosion in lithium bisperfluoroethylsulfonyl imide — $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$.

2. Experimental

The new perfluoroalkylsulfonyl imides lithium salts were purified and pre-dried before the testing. A typical purity of the salts investigated here were in the range of 99.5 to 99.9% molar purity as determined by ^{19}F and ^1H NMR analysis. LiPF_6 used for comparison was from Hashimoto Chemical.

Pure aluminum electrodes (99.999%) were used for the three-electrode corrosion and scanning voltammetry experiments. 99.5% pure aluminum disks were used as the cathode current collectors in the coin cells arrangements. The electrode potentials were measured against lithium flag electrode in the same solution.

The X-ray photoelectron spectroscopy (XPS) spectra were taken using a Surface Science Laboratories Model SSX-100-01 M-probe ESCA spectrometer which makes use of an $\text{Al K}\alpha$ monochromatic X-ray excitation source. The area analyzed on each sample was approximately $300\ \mu\text{m}$ in diameter. Compositional depth profiles were obtained on each specimen by sequentially sputter etching the surface using an Ar^+ ion beam and recording the appropriate XPS spectra. Ion etching

was accomplished using a Kimball Physics ILG-2 differentially pumped ion gun operated at 2.5 KeV beam energy. The sputtering rate for these materials is approximately 25 Å/min.

3. Results and discussion

The magnitude of the problem of aluminum corrosion associated with LiTFSI and the more commonly known lithium triflate is presented in Fig. 1. Under a potentiostatic condition of 4.2 V (versus Li/Li⁺) pure aluminum (polished in an argon-filled dry box under hexane) can develop dissolution current densities in excess of 10 mA/cm² in propylene carbonate (PC) containing 1 M LiTFSI and in excess of 20 mA/cm² for LiSO₃CF₃. Also shown in Fig. 1 are chronoamperometric responses of aluminum of two new members of this sulfonyl imide family and also the response of Al in 1 M LiPF₆. Surprisingly, the corrosion current density, measured after 1 h at 4.2 V is approximately 2.5 μA/cm² for the perfluoromethylbutyl analog and about 1 μA/cm² for the bis-perfluoroethyl analog of LiTFSI, lithium bisperfluoroethylsulfonyl imide. This current density is comparable with the experiment using LiPF₆ as the electrolyte salt. Thus expansion of the perfluoroalkyl group from –CF₃ to –C₂F₅ has about a four order of magnitude effect on the corrosion current density.

Microscopic examination of aluminum surfaces corroded in 1 M LiTFSI/PC reveals a high density of multi-micron size pits. A useful measure of the tendency of aluminum to form corrosion pits is the determination of a protection poten-

tial (E_p), the potential below which pits are repassivated [5]. It is possible to operate the electrode above this protection potential without initiating pits but existing pits will propagate above E_p . Protection potentials for aluminum in these lithium salts have been determined using cyclic voltammetry in a three-electrode cell. The scan rate used was 0.5 mV/s and the potential was ramped to a sufficiently positive potential to induce pitting corrosion and then reversed. Fig. 2 presents these results in tabular as well as voltammetric form. Fig. 2 shows that extension of the perfluoroalkyl groups on the sulfonyl imide from –CF₃ to –C₂F₅ shifts the pitting potential by about 1 V. Protection potentials of the perfluoromethylbutyl and bis-perfluoroethyl analogs are high enough to include these materials as potentially attractive alternatives to LiPF₆ in high voltage lithium-ion cells.

The conductivity of some of the sulfonates and sulfonyl imides discussed above are shown in Fig. 3. While LiN(SO₂C₂F₅)₂ is less conductive than LiPF₆ it is comparable with LiN(SO₂CF₃)₂. The difference most likely is due to the considerably larger anion of the sulfonyl imides although transference number measurements have not been undertaken as yet.

The thermal stability of LiN(SO₂C₂F₅)₂ is representative of the sulfonyl imides in general and is shown along with LiPF₆ in Fig. 4. Essentially no weight loss was observed, under nitrogen, up to approximately 350 °C. The LiPF₆ results can be influenced by the presence of moisture and this may be the reason we have observed lower temperatures for the onset of decomposition compared with others [1].

The cycling properties of the new salts were tested in a 1225 coin cell using LiCoO₂ as the positive and Conoco XP3

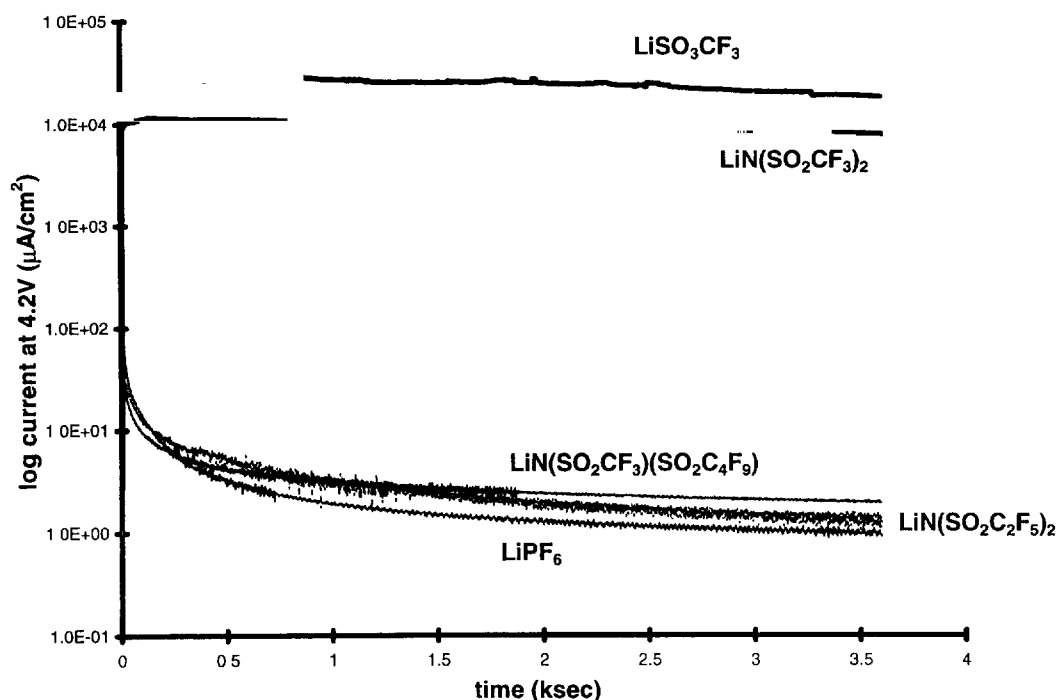


Fig. 1 Aluminum corrosion current density at 4.2 V (vs. Li/Li⁺) in 1 M PC solutions of various lithium salts showing a difference between the perfluoromethyl and perfluoroethylsulfonyl imides.

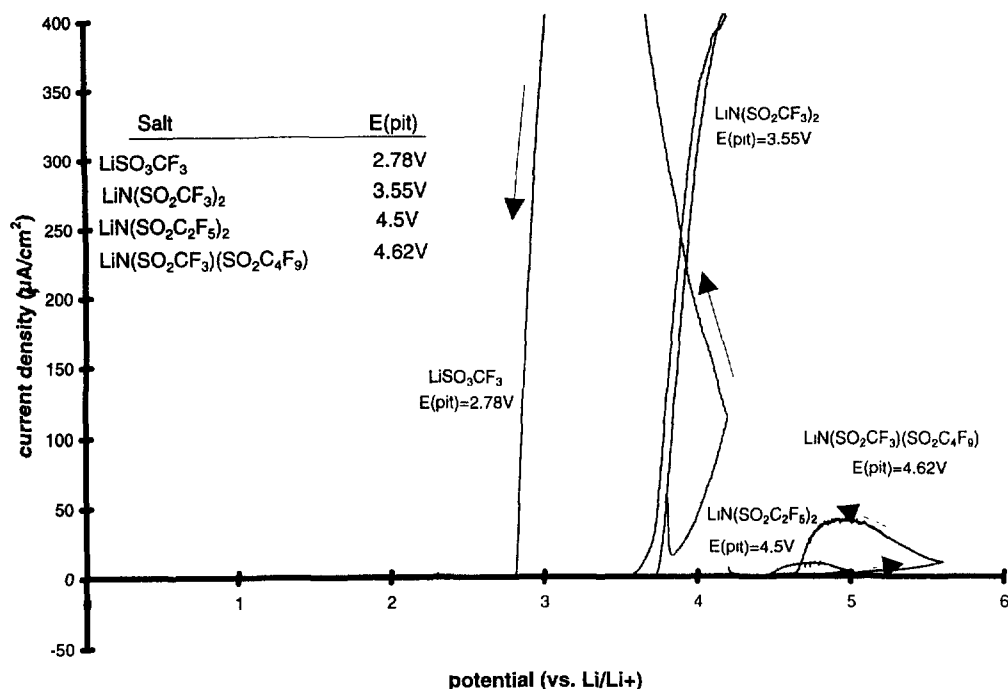


Fig. 2. Pitting potential of various sulfonates and sulfonyl imides at aluminum. All electrolytes 1 M in EC-PC (1:1 v/v) and taken at a scan rate of 0.5 mV/s

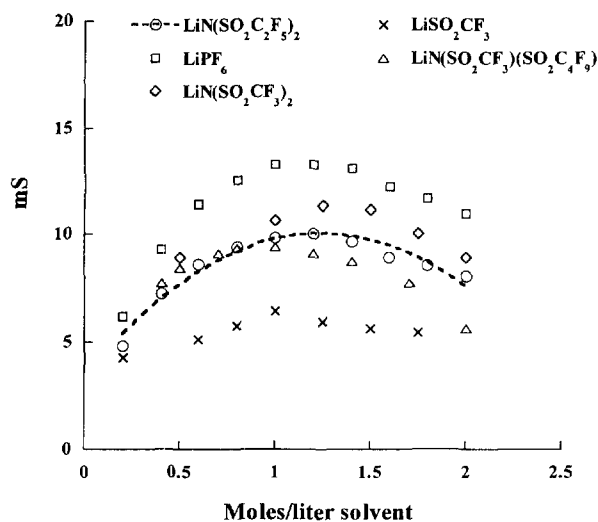


Fig. 3. Conductivity of salts in PC-DME (1:1 v/v) as a function of salt concentration at room temperature.

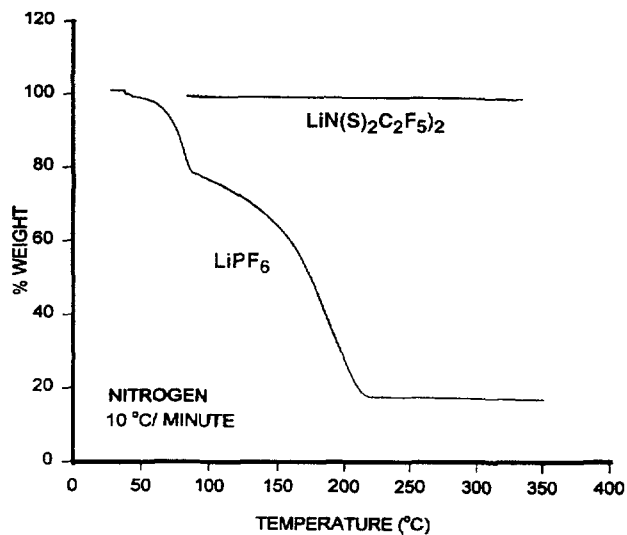


Fig. 4. Thermal gravimetric analysis of the perfluoroethylsulfonyl imide salt and LiPF₆.

coke as the negative materials. The cells were charged under a constant voltage of 4.2 V with a current limit of 4 mA/cm² and a charge cutoff current of 200 μ A/cm². Discharge was done under a constant current of 1 mA/cm². Every tenth cycle the cells were held at 4.2 V for a 24 h period before discharging. This cycling procedure was adopted to assure the cycling performance is not affected by unexpected aluminum corrosion. Typical results are given in Fig. 5. While the results indicate better performance of the sulfonyl imides compared with LiPF₆, it is premature to definitively assign better capacity retention of the new salts over LiPF₆.

In an attempt to better understand the differences in aluminum corrosion observed amongst the various electrolytes

we have begun XPS surface analysis of aluminum polarized at high potentials. The significant differences observed in the pitting potentials for the sulfonyl imides and sulfonates might be elucidated by an examination of the chemical composition and thickness of the passivation layer.

In general samples for XPS analysis were obtained by building 1225 coin cells with a lithium metal negative electrode and a 99.5% pure aluminum disk as the positive electrode. The aluminum was polished in a dry room under hexane. A standard porous polyethylene membrane was used as a separator and the cell was filled with 40 μ l of the desired electrolyte. The cells were potentiostated at 4.2 V for 8 h periods and then disassembled for analysis. The aluminum

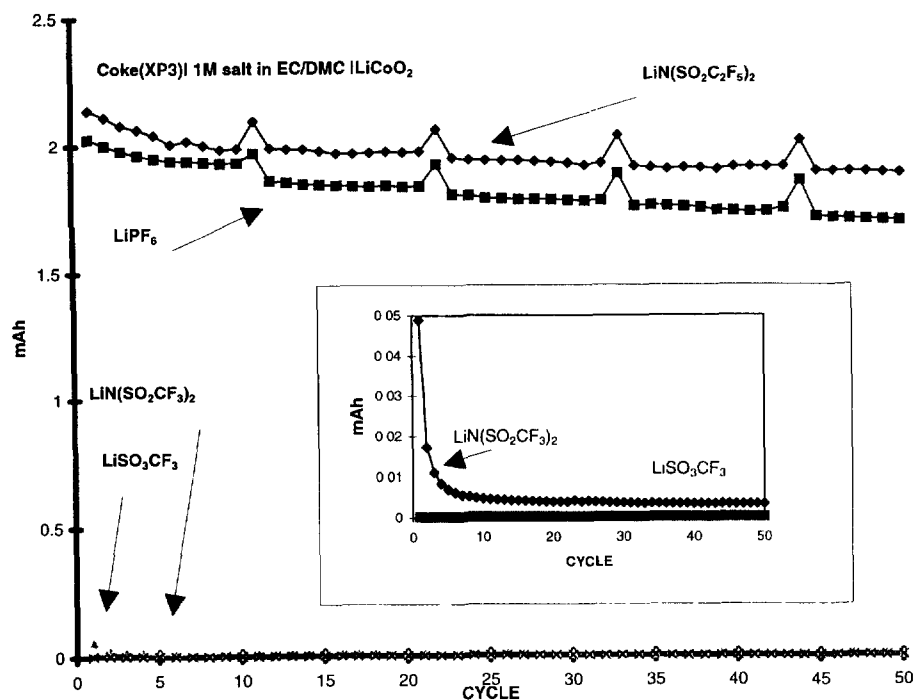


Fig. 5. Cycling results of 1225 coin cells with aluminum positive electrode current collectors, 1 M solvent (EC-DMC 1:1 v/v).

disk current collectors were mounted on the XPS sample holder in an argon-filled glove box and transported to the XPS vacuum chamber in a UHV compatible specimen transfer vessel back-filled with the glove box atmosphere.

A compositional depth profile and a relative atomic abundance/composition of the passivation layers is given in Fig. 6 and Table 1, respectively. On the aluminum sample polarized in 1 M LiTFSIPC (Fig. 6(a)) aluminum and oxygen are found throughout the surface layer in relative atomic abundance consistent with Al_2O_3 . Also found were relatively high levels of lithium and fluorine at relative abundance consistent with LiF (Table 1). $\text{Al}^{(0)}$ is also observed as well as aliphatic carbon.

The surface layer of aluminum polarized in $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ is apparently much thinner than the layer generated in LiTFSI (Fig. 6(b) and Table 1) as indicated by the relative abundance of $\text{Al}^{(0)}$ at short sputtering times. Furthermore the Li^+ and F^- signals drop off very quickly in the surface layer as does the signal for carbon associated with carbonate. This carbonate may exist as either $\text{Al}_2(\text{CO}_3)_3$ or Li_2CO_3 and likely arises from the reduction of the solvent, PC, by Al^+ intermediates.

Unlike the layer found from the imides the surface layer of aluminum generated in LiPF_6 electrolyte has significant amounts of carbonate throughout most of the layer (Fig. 6(c)). Al_2O_3 and small amounts of LiF are also

Table 1
Summary of ESCA quantitation and peak-fitting data^a

	Etch time (s)	Atomic %						
		C-C	CO_3^{2-}	O	Al^{3+}	Al^0	Li^+	F^-
LiPF_6	20	21	4.0	37	14	4.0	13	7.0
	320	n.d.	4.8	30	11	35	13	5.8
	500	n.d.	3.7	27	10	45	11	3.3
	980	n.d.	n.d.	12	9.0	77	n.d.	1.8
$\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$	20	15	5.0	30	12	9.1	20	8.7
	320	2.2	n.d.	23	16	56	n.d.	3.1
	500	2.1	n.d.	20	14	62	n.d.	2.2
	980	0.8	n.d.	17	12	68	n.d.	1.9
$\text{LiN}(\text{SO}_2\text{CF}_3)_2$ (LiTFSI)	20	37	n.d.	9.1	5.1	6.8	21	21
	320	7.6	n.d.	17	12	34	14	15
	500	4.9	n.d.	16	12	43	13	11
	980	1.5	n.d.	15	11	59	5.4	7.7

^a ESCA: electron spectroscopy for chemical analysis

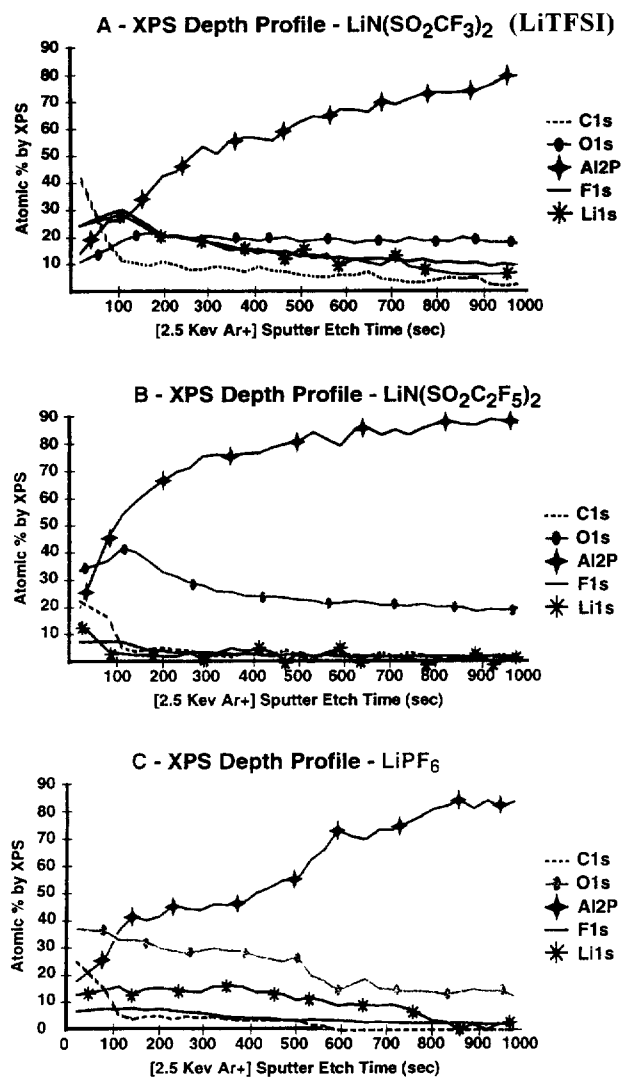


Fig. 6. XPS depth profiles of the passive layers on aluminum formed at 4.2 V vs. Li/Li^+ in PC (a) $\text{LiN}(\text{SO}_2\text{CF}_3)_2$; (b) $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$, and (c) LiPF_6 .

observed. Recently other workers have performed similar analysis on aluminum polarized in PC solutions of 1 M LiPF_6 [6] and they concluded that the passive surfaces were composed mainly of Al_2O_3 and AlF_3 . It appears that the presence of AlF_3 was based primarily on the XPS fluorine peak at 686.5 eV. As shown in Table 1 we have also observed significant levels of fluorine but the presence of lithium and the relative abundance of the two elements suggests the presence of LiF rather than AlF_3 . It appears from this preliminary analysis that the high level of corrosion observed at aluminum in electrolytes containing LiTFSI stems from a relatively porous, diffuse passive layer where the high levels of LiF , perhaps, contribute to the disorder and porosity of the otherwise dense and protective Al_2O_3 and carbonate-containing layer found in Al samples polarized in LiPF_6 or $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$.

Others have suggested that a passive layer rich in fluoride is highly passivating and that this explains the high degree of

corrosion resistance seen in electrolytes containing LiPF_6 [7]. One could expect that aluminum polarized in LiPF_6 -containing electrolytes would attain a passive layer which would persist when polarized in, for example, LiTFSI. In order to check the protective properties of such a layer an aluminum sample was polarized in 1 M LiPF_6/PC for 1 h. The current at the end of this hour had dropped to below $1 \mu\text{A}/\text{cm}^2$. The electrode was then polarized in 1 M LiTFSI at 4.2 V for 1 h. Fig. 7 indicates that the passive layer generated in the LiPF_6 electrolyte does not protect against aluminum dissolution in 1 M LiTFSI. This observation suggests a reaction of the TFSI anion at these voltages, which is not seen at glassy carbon electrodes, as the initiating step in aluminum dissolution.

The fundamental basis for the instability of some perfluorosulfonates and perfluoroalkylsulfonyl imides on aluminum at oxidizing potentials is not completely clear at this time. However, a general mechanism based upon the experimental observations can be postulated. The wide variation of the protection potentials (Fig. 2) seems to be correlated to the molecular weight of the anion and thus the size of the anion. Also when corrosion does occur, small levels of S^{2-} are detected in the surface films. This observation is only explained by the reduction of the anion by Al^+ species which have been indicated as intermediates in the oxidation of Al metal to Al^{3+} [8,9]. Upon polarization of the aluminum at high potentials these highly reactive intermediates are formed and can migrate or diffuse to the vicinity of the surface film/electrolyte interface where they can react with either adsorbed PC or the anions. In LiPF_6 electrolytes the XPS data suggests that reduction of the solvent, PC, is occurring to yield carbonates and that relatively little fluoride compared with the LiTFSI example is formed. The reductive reaction with PF_6^- anion may not be as facile as with the sulfonates and sulfonyl imides thereby favoring the reduction of the solvent molecules and the creation of more dense, less porous, oxygen rich surface films. The relatively high levels of LiF found in the surface polarized in LiTFSI/PC suggests to us that this material, while highly insoluble, may be introducing sufficient disorder into the surface layer so as to enhance porosity and thus transport through the layer. The reaction with the sulfonyl imide and sulfonate anions is favored when the density of the anions adsorbed onto the film surface is high and when the anion concentration within the surface film is high, both conditions favored by smaller anions.

4. Conclusions

New lithium bis-perfluoroalkylsulfonyl imide salts, recently synthesized in our laboratories, exhibit high protection potentials at aluminum. A corrosion mechanism of aluminum was postulated in which a correlation of the molecular weight of the anions to their protective properties was established. Along with the excellent thermal and hydrolytic stability, the good conductivity and cycling characteristics

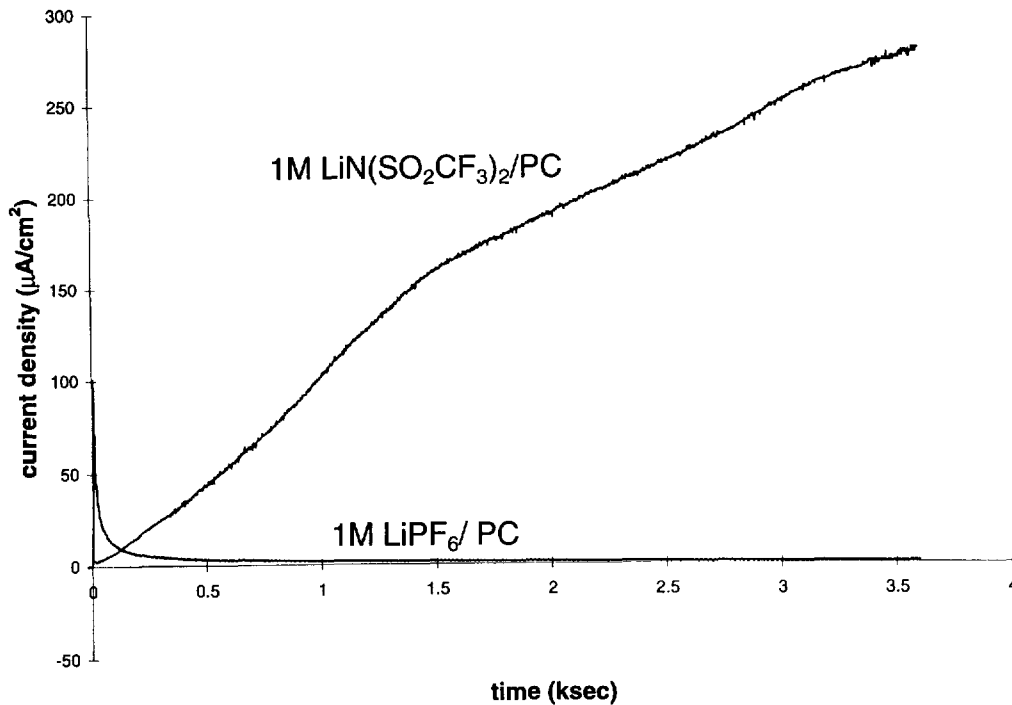


Fig. 7. Corrosion current density of aluminum electrode polarized in 1 M LiTFSI at 4.2 V after being previously polarized in 1 M LiPF₆ for 1 h at 4.2 V

achieved in typical lithium-ion test cell, the new salts seem to be promising candidates for practical batteries.

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