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On the Surface Chemical Aspects of Very High Energy Density, **Rechargeable Li–Sulfur Batteries**

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Li(metal)-sulfur (Li-S) systems are among the rechargeable batteries of the highest possible energy density due to the high capacity of both electrodes. The surface chemistry developed on Li electrodes in electrolyte solutions for Li-S batteries was rigorously studied using Fourier transform infrared and X-ray photoelectron spectroscopies. A special methodology was developed for handling the highly reactive Li samples. It was possible to analyze the contribution of solvents such as 1-3 dioxolane, the electrolyte $LiN(SO_2CF_3)_2$, polysulfide (Li_2S_n) , and $LiNO_3$ additives to protective surface films that are formed on the Li electrodes. The role of LiNO₃ as a critical component whose presence in solutions prevents a shuttle mechanism that limits the capacity of the sulfur electrodes is discussed and explained herein. © 2009 The Electrochemical Society. [DOI: 10.1149/1.3148721] All rights reserved.

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Li-sulfur batteries have attracted the attention of the electrochemistry community for more than 3 decades ever since the onset of interest in research and development of rechargeable Li batteries.^{1,2} Sulfur can undergo reversible reduction to Li_2S , which means a theoretical capacity of about 1675 mAh/g, which is among the highest values possible for cathodes to rechargeable Li batteries. The lithiation of sulfur is a multistage process in which several intermediate Li_2S_n species are formed around two main redox potentials: between 2.4 and 2.3 V (25% of capacity) and between 2.1 and 2 V (75% of capacity) vs Li/Li^{+,3} Due to the relatively low redox potential of sulfur cathodes (compared to most of the commonly used Li insertion cathodes based on lithiated transition-metal oxides), it is important to use Li metal anodes in Li-S cells to obtain the maximal voltage with these systems. The use of Li anode forces the use of electrolyte solutions based on ethereal solvents due to their acceptable low reactivity toward lithium metal.⁴ The use of ethereal solvents, whose anodic stability is limited (3-4 V vs Li/Li^{+}),⁵ is indeed possible in Li–S systems, thanks to the relatively low redox potential of sulfur electrodes. Over the years, we can see continuous work on Li-S battery systems⁶⁻¹² and on Li batteries in which the cathodes comprise sulfur-containing polymers (mostly with S-S groups).¹³⁻¹⁶ The use of Li metal as an anode limits the cycle life of any rechargeable Li (metal) battery system due to dendrite formation upon charging (Li deposition), which may cause short circuiting of the battery and loss of active mass due to the electrical disconnection of Li dendrites from the bulk. The best solvent for rechargeable Li (metal) batteries was 1-3 dioxolane (DOL).¹⁷ The surface chemistry of Li metal in DOL solutions is complicated. DOL is reduced to several ROLi species and oligomers with -OLi edge groups.¹⁸⁻²⁰ The latter species add some flexibility to the protective, passivating surface films formed on Li in DOL solutions that probably enables their accommodation to the morphological changes in Li during the course of charge-discharge cycling (Li deposition/dissolution processes).

In the past, there were some efforts to commercialize rechargeable Li (metal) batteries, such as Li-Li_{0.33}MnO₂ (based indeed on DOL solutions).^{21,22} However, rechargeable Li (metal) cells based on Li insertion cathodes could not compete with Li-ion battery technology, mostly due to limitation in cycle life and the need for long charging time, and thus were abandoned. The main factor that limited the performance of Li-Li_{0.33}MnO₂ cells was the continuous reaction of lithium with the electrolyte solutions, which led to their detrimental depletion (no dendrite formation), especially upon fast charging conditions.²

Similar limitations are also expected for Li-S cells. However, their extremely high capacity definitely justifies the commercialization of rechargeable Li (metal)-sulfur batteries although their cycle life should be shorter compared to that of Li-ion batteries. A critical problem of Li-S cells is the shuttle mechanism that limits the full rechargeability of the sulfur cathodes: Full oxidation of polysulfide species such as Li₂S₆ to sulfur upon charging is avoided due to cyclic processes in which these moieties are reduced by lithium to species such as Li₂S₄. Hence, the charging process involves the oxidation of Li_2S_4 to Li_2S_6 as the main and dominant reaction, which means a realization of no more than 50-75% of the full capacity.²⁴ It was recently found that the use of LiNO₃ as an additive to the electrolyte solutions in Li-S batteries prevents this detrimental shuttle mechanism.4

This work is aimed at understanding the surface chemistry of Li electrodes in various electrolyte solutions for Li-S batteries that contain the components DOL, LiN(SO₂CF₃)₂ (LiTFSI) as the electrolyte, Li₂S_n, and LiNO₃. A special methodology was developed for the preparation and study of the highly sensitive Li samples. Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) were used as the spectroscopic tools for this work.

Experimental

Li battery grade DOL (Ferro, Tomiyama), LiN(SO₂CF₃)₂ (3 M), and LiNO₃ (Aldrich) were used as received. Li rods for the spectral studies, 1.25 cm thick, were obtained from Chemetall Foote Corporation (Kings Mountain, NC, USA). Li₂S₆ was prepared by adding stoichiometric amounts of lithium (Chemetall Foote Corp., 0.5 mm thick lithium foil, >99.9%) and sulfur (Alfa Aesar, sublimed sulfur powder -100 mesh, 99.5% assay) in dioxolane (Ferro, 99.98 % min) to produce 13 wt % Li_2S_6 in this solvent. The mixture was tightly capped and stirred vigorously for 18 h at 50°C at which time all the Li and S reacted. Elemental analysis by inductively coupled plasma confirmed the stoichiometry and quantity of polysulfides. The usual concentrations of the various components in the DOL solutions used herein were 0.38 M LiTFSI, 0.31 M LiNO₃, and 0.23 M Li₂S₆ (mol/L). The water contamination level was measured by a Metrohm Inc. (Denmark) KF titrator.

Electrochemical measurements (chronopotentiometry, voltammetry, and electrical impedance spectroscopy) were carried out using multichannel computerized equipment from Maccor, Arbin, and Solartron (FRA model 1255 plus multichannel potentiostat/galvanostat system, model 1470). Impedance spectra of Li electrodes were measured within the 100,000-0.01 Hz range, with a voltage amplitude of 5 mV around 0 V (Li/Li⁺). The behavior of sulfur electrodes in DOL solutions containing LiNO₃ and in LiNO₃ free solutions was measured extensively by Sion Power Inc. in Li-S cells prepared therein, as demonstrated previously.^{24,25} The cathodes were prepared

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by coating a mixture of 73 parts of elemental sulfur (available from Aldrich Chemical Company, Milwaukee, WI), 16 parts of a conductive carbon pigment Printex XE-2 (a trademark for a carbon pigment available from Degussa Corporation, Akron, OH), 6 parts of a second conductive pigment, Ketjenblack (available from Akzo Nobel, The Netherlands), and 5 parts of polyethylene powder (grade T1000 available from Baker Hughes, Barnsdall, OK) dispersed in isopropanol onto a 7 µm thick conductive carbon-coated aluminum foil substrate. After drying, the coated cathode active layer thickness was about 40 µm. The anodes were lithium metal (>99.9% Li, 2 mil thick foil from Chemetall Foote Corp., Kings Mountain, NC). The porous separator used was 9 µm Setela (a trademark for a polyolefin separator available from Tonen Chemical Corporation, Tokyo, Japan and also available from Mobil Chemical Company, Films Division, Pittsford, NY). The above components were assembled in a layered structure of cathode/separator/anode, which was folded in half making a bicell, and placed in a foil pouch with liquid electrolyte (approximately 0.32 g). The electrolyte solutions used were mixtures of 10 parts of lithium bis(trifluoromethane sulfonyl) imide, (lithium imide available from 3M Corporation, St. Paul, MN), 2 parts lithium nitrate (available from Aldrich Chemical Company, Milwaukee, WI), and 4 parts lithium hexasulfide (synthesized as described above) in DOL (available from Ferro Corporation, Independence, OH), with water content of less than 20 ppm. The bicells had an electrode area of about 33 cm². The sulfur content in the cell was 40 mg, equivalent to 67 mAh capacity (1675 mAh/g \times 0.04 g). After sealing the cell in a foil pouch, it was stored for 24 h and then tested. Discharge-charge cycling of the cell was performed at 13.7 mA/7.8 mA, respectively (corresponding to current densities of 0.42 and 0.24 mA/cm²), with a discharge cutoff at a voltage of 1.7 V and a charge cutoff at 2.5 V.

Impedance measurements of Li metal foil (Chemetall Foote Corp., 1 mm thick) electrodes were carried out using two electrode parallel-plate cells (Li working and counter electrodes), in which Li foils were pressed by stainless steel bars into polypropylene frameworks that included inlets for solutions. For FTIR measurements we used a Magna 860 spectrometer from Nicolet, placed in a glove box, under H₂O and CO₂ free atmosphere that was maintained using condensed air treated by a regular Balston Inc. (England) system. Surface spectra from Li electrodes were measured ex situ in the reflectance mode using an UpIR: Upward looking diffuse reflectance accessory from Pike Technologies. The oxidation state of the surface species of the Li metal electrodes was analyzed by XPS. Electron spectra were obtained with a Kratos Axis-HS spectrometer (England) (residual gas pressure of $\sim 5 \times 10^{-10}$ Torr) using monochromatized Al K α radiation ($h\nu = 1486.68 \text{ eV}$) and a hemispherical analyzer. High resolution spectra were recorded with an X-ray generator operating at 15 kV and 5 mA and a pass energy of 40 eV (0.05 eV steps were applied for its acquisition). The X-ray beam may change the chemical nature of the surface, especially in the present study, in which the substrates were highly reactive Li metal surfaces. Thereby, measurements of each sample were always repeated three times. For all the samples studied, no significant changes in the spectra were detected at the operating condition chosen. Hence, the data presented herein indeed reflect the surface species formed on lithium in the solutions studied in this work. During measurements, the vacuum in the analysis chamber was 2 \times 10^{-9} Torr. Binding energies (BEs) were corrected with respect to the BE value of the C 1s peak at 284.8 eV. The Shirley background, the mixed Gaussian/Lorentzian approach, was used for the fitting of the high resolution O 1s, N 1s, C 1s, S 2p, and Li 1s peaks by the Vision 2 software (Kratos). We developed a special methodology for the preparation of Li electrodes in solutions and their further handling without exposing them to atmospheric contaminants. We developed a special methodology for the preparation and handling the highly reactive and sensitive Li surfaces so the spectral information measured herein should be fully authentic and reliable. All preparations of the Li electrodes were carried out in a home-made glove



Figure 1. Presentation of special arrangements for Li sample preparation and their spectral studies. (a) The apparatus for Li sample preparation in solutions. (b) The cell for FTIR spectroscopy (measured using diffuse reflectance attachment (see Experimental section). (c) The transfer system that takes Li samples from the special glove box to the XPS spectrometer.

box that could be fully evacuated, whose atmosphere was treated by O_2 , H_2O , and an organic species removal system from M. Braun Inc. (the same system as made for regular glove boxes of this company). Before each single step of Li sample preparation, the glove box was evacuated to $10^{-2}-10^{-3}$ Torr and was refilled by ultrapure argon (Oxygen Center, Israel). More details about such an operation with evacuable glove boxes were provided elsewhere.²⁶

Shiny and reflective disks (1.25 cm wide and 1 mm thick) were freshly prepared in solutions by the knife and the cell (filled with solution) presented in Fig. 1a. After the appropriate storage in solution, the sample was washed three times with pure DOL and dried. It was confirmed by FTIR spectroscopy that this treatment removed traces of soluble Li salts from the surface. The surface films formed on it in solution were analyzed by FTIR spectroscopy and XPS. For the FTIR measurements, the Li disks were hermetically closed in the cell presented in Fig. 1b, pressed toward its KBr window. This cell was introduced into the FTIR spectrometer glove box and placed facing downward on the reflectance accessory. For XPS measurements, we used the home-made transfer system presented in Fig. 1c, which contained a magnetic manipulator (attached to a sample holder), a gate valve, and a flange that fit both the entry port of the XPS spectrometer and a similar entry port built in the above special glove box. Hence, the Li samples were exposed fresh to solutions, then to highly pure argon atmosphere, and finally to the high vacuum of the XPS spectrometer $(10^{-8}-10^{-9} \text{ Torr})$. To obtain reliable and reproducible spectra for these ultrasensitive samples, the glove box needed to be evacuated and refilled with ultrapure argon before each step of sample preparation, and each single sample had to be handled separately.

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Figure 2. Typical voltage profiles of Li–S cells (pouch cells) comprising a Li metal anode, a sulfur cathode (composite electrodes containing the active material, carbon, and current collector), and a DOL-based solution at 30°C: (a) DOL and 0.38 M LiN(SO₂CF₃)₂ and (b) DOL and 0.38 M LiN(SO₂CF₃)₂-0.31 M LiNO₃. See details on preparations and cycling conditions in the Experimental section.

Results and Discussion

On the effect of $LiNO_3$ in solutions on the behavior of Li-S cells.— A detailed description and discussion of the characteristics and performance of sulfur electrodes in the above-mentioned electrolyte solutions is beyond the scope of this paper. However, it is important to demonstrate herein the important effect of the presence of $LiNO_3$ in solutions, on the behavior of sulfur electrodes in these systems, because a main goal of the present study was to discover the effect of this additive on the surface chemistry of Li electrodes.

Figure 2 shows the typical, steady-state, potential profiles of two Li–sulfur cells (prepared by Sion Power Inc.) in galvanostatic cycling. The electrolyte solution in one of the cells comprised DOL and 0.38 M LiN(SO₂CF₃)₂ while the solution in the other cell contained in addition to these components 0.31 M LiNO₃. Upon cycling, polysulfides are formed and introduced to the electrolyte solution. The profile of the sulfur electrode in the cell which contained LiNO₃ clearly shows a high reversible capacity around 1150 mAh/g and the two expected plateaus at 2.4–2.3 and 2.1–2 V (vs Li counter electrode) related roughly to the following processes

$$3S_8 + 8Li^+ + 8e^- \rightleftharpoons 4Li_2S_6$$
^[1]

$$Li_2S_6 + xLi^+ + xe^- \rightleftharpoons (6 - y)Li_2S + yLi_2S_2(8 < x < 10),$$

 $y = 0 - 1$ [2]

In fact Eq. 1 and 2 is a very simplified description of the complicated electrochemical behavior of these electrodes (see Ref. 24 for a detailed discussion). Note, however, that when the solution in these Li–S cells contains LiNO₃ the cells can be fully charged to reach the high capacity of sulfur electrodes.

In the absence of LiNO₃ in solutions, the process around 2.4–2.3 V could not be reached upon charging, and the maximal capacity measured in the present study could not exceed 650 mAh/g due to the shuttle mechanism discussed in Ref. 24 and 25. Voltammetric studies of the above electrolyte solutions with noble-metal electrodes do not show any pronounced redox activity at potentials above 1.8 V, in which sulfur electrodes are electrochemically active. Hence, the main impact of this additive belongs to the Li side.

Impedance spectroscopic studies.— The effect of the presence of LiNO₃ in solutions on the Li surface chemistry was well demonstrated by impedance spectroscopic measurements of Li electrodes in these solutions. Figure 3 presents impedance spectra (Nyquist plots) of Li electrodes prepared and stored for 18 h in DOL/0.38 M



Figure 3. Impedance spectra of Li electrodes prepared fresh in DOL/0.38 M LiTFSI, DOL/0.38 M LiTFSI/0.31 M LiNO₃, DOL/0.38 M LiTFSI/0.23 M Li₂S₆, and DOL/0.38 M LiTFSI/0.31 LiNO₃/0.23 M Li₂S₆ solutions as indicated, measured after 18 h of storage open circuit voltage presented as Nyquist plots.

LiTFSI, DOL/0.38 M LiTFSI/0.31 M LiNO₃, DOL/0.38 M LiTFSI/0.23 M Li_2S_6 , and DOL/0.38 M LiTFSI/0.31 LiNO₃/0.23 M Li₂S₆ solutions as indicated. The solution contained less than 10 ppm of trace water (measured by KF titration). The specific conductivities of these solutions at 25°C were measured separately (Pt electrodes) and were 1.3, 1.9, 2.04, and 2.7 mS/cm, respectively. The spectra in Fig. 3 comprise flat semicircles (note the difference in the scales of the Z' and Z'' axes) at the high medium frequencies as their main feature and a straight or slightly curved line at the low frequencies. The Z' values in these spectra, measured at the highest frequencies (i.e., the extrapolated intercept of the high frequency semicircle with the Z' axis), may reflect the solution impedance. Hence, the ratios between the high frequency Z' values measured with different solutions should be similar to the reciprocal of the ratios between the specific conductivity values of the solu-This is indeed the case for DOL/LiTFSI tions. and DOL/LiTFSI/LiNO3 solutions. However, when the solution contains both polysulfide (PS) and LiNO₃ the picture is complicated because of the surface reactions of Li in these solutions (as discussed later), which may considerably change the concentration of conductive species in them. Initially (soon after preparation in solutions), the impedance of the Li electrodes in solutions is much smaller and it gradually increases upon storage, until reaching steady-state values after about 24 h of storage in these solutions (very similar to what is presented herein). Impedance spectra of Li electrodes were studied rigorously in the past.^{27,28} The big, flat semicircle is attributed to multilayer surface films that are formed in solutions on the active metal due to its continuous reactions with solution species. These reactions stop when the surface films become thick enough, to avoid electron transfer through them, from the Li to the solution species. The multilayer structure of the surface films is due to an expected gradient in the oxidation states of the surface species: Species with the lowest oxidation state should be formed close to the Li side (e.g., Li₂O, LiH, Li₃N, Li₂S, and species with Li-C bonds), while surface species close to the solution side may possess higher oxidation states (e.g., species with Li alkoxy groups, carbonyl groups, and S=O bonds). All ionic compounds of lithium (e.g., Li oxide, hydroxide, carbonate, halide, and organic Li salts) can conduct Li ions under an electrical field. Thereby, the surface films formed on lithium in most of the polar-aprotic solutions are in fact Li-ion conductors. They may protect Li electrodes from corrosion by blocking electron transfer but allow transport of Li ions by migration under electrical field, thus behaving as solid electrolyte interphase (SEI) between the active metal and the solution (the so-called SEI model²⁹). The flat semicircles that characterize impedance spectra of Li electrodes in most of polar-aprotic solutions can be modeled by parallel RC circuits in series (the "Voigttype" equivalent circuit analog, R-resistor and C-capacitor connected in parallel) and reflect in fact the resistance(s) for Li-ion migration via the multilayer surface films, coupled with the film capacitance, as previously discussed.²⁷ The low frequency part of

v c-o (ROLi)

(ROLi)

1400

HCO₂Li

bending

HCO₂Li

400

3400 2400 1400 400 **Wavenumber cm⁻¹** Figure 4. FTIR spectra of Li surfaces (measured ex situ) prepared and stored for 2 min in much 201 and in a DOL (LITESL 0.22 M solution [(a) and (b)

V CH (ROLi)

a)

νон

LiOH

V он (ROH)

3400

b)

v_{oh} (ROH)

(ROLi)

HCO₂Li

2400

Wavenumber cm⁻¹

HCO₂L

0.0035

0.0025

0.0015

0.0005

-0.0005

0.0035

0.0025

0.0015 0.0005 -0.0005

Absorbance

Absorbance

for 2 min in pure DOL and in a DOL/LiTFSI 0.38 M solution [(a) and (b), respectively]. Peak assignments are presented on their spectra.

these spectra, which resemble "Warburg-type" elements, probably relates to the Li-ion diffusion processes at the porous surface filmsolution side.²⁷ The spectra in Fig. 3 reflect a very strong effect of the solution composition on the electrodes' impedance. It is spectacular in Fig. 3 that the presence of either LiNO₃ or Li₂S₆ in DOL/ LiTFSI solutions remarkably decreases the impedance of the Li electrodes in solutions. However, the presence of LiNO₃ in solutions containing Li₂S₆ leads to a higher Li electrode impedance, compared to what is measured in the LiNO₃-free (Li₂S₆-containing) solutions. This can be naturally interpreted as a pronounced effect of additives such as LiNO₃ and Li₂S₆ on the Li surface chemistry, which leads to the formation of surface films with different transport properties (for Li ions). A quantitative study of these impedance

Table I. Spectral bands and peak assignments of spectra obtained from Li electrodes prepared in DOL. Peak locations are in cm⁻¹ units. Peak assignments are based on Ref. 18-23, 30, and 31.

| Li surface prepared and stored in DOL for a few minutes | Li surface prepared and stored in DOL for hours/days | Peak assignments |
|---|--|---------------------------------|
| 2960 (m) | 2945 (w) | v _{as} CH ₂ |
| 2880 (m) | 2883 (w) | $\nu_{s}CH_{2}$ |
| | 2700 (w) | vCH Li formate |
| | 1662 (s) | $\nu C = O$ Li formate |
| | 1500-1450 | Li carbonate |
| 1440-1300 (m) | 1440-1300 (m) | $\delta C-H (CH_2, CH_3)$ |
| 1200 (w) | 1200 (w) | (δ) various bending |
| | | modes |
| 1150 (s) | 1150 (w) | νC–O |
| 1100–1000 (s) | 1100-1000 (s) | νC–O |
| | 880 (s) | Li carbonate |
| 849 (m) | | And various bending modes |
| | 750–770 (m) | Li format (bending) |
| | 700 (s) | Li ₃ N |
| | | 5 |

Table II. Major peaks related to LiTFSI reduction products appearing in spectra obtained from Li electrodes and noble metals at low potentials treated in $LiN(SO_2CF_3)_2$ -DOL solutions. (Peak assignments are also presented. This table provides data on all the main IR peaks related to LiTFSI and the reduction products of TFSI anion in the presence of Li ions.)³⁰⁻³²

| Reference compound [The neat salt $LiN(SO_2CF_3)_2$ (TFSI)] | Li metal electrode prepared in DOL/ LiTFSI solutions | Peak assignments |
|---|--|----------------------------------|
| 1330 | 1350 | vSO ₂ –N |
| | | (sulfone amide) |
| 1245 | 1300-1320 | $\nu_{as}SO_2$ |
| | 1231 | (sulfone) |
| 1196 | | vC-F |
| 1140 | 1189 | ν -SO ₂ (sulfone) |
| | 1139 | 2 () |
| 1062 | | νS=O |
| | 1062 | vS-O |
| | | δ (bending modes) |
| 795 | 886 | CF ₃ , C-S, S-O, etc. |
| 745 | 786 | <u>.</u> |
| 647 | | Li ₂ O |
| 604 | 650 | 2 |
| 576-513 | | νLiO |
| | | |

spectra is beyond the scope of this work, especially in light of the fact that in many cases, impedance spectroscopy cannot provide unambiguous information when used as a main analytical tool for electrochemical systems. Hence, it was interesting to investigate the possible effects of the presence of $LiNO_3$ and Li_2S_6 in solutions on the surface chemistry of Li electrodes by spectroscopic means that may provide specific information (FTIR and XPS).

FTIR measurements.- Li electrodes were prepared and stored in various solutions during different periods of time (from minutes to weeks). Several sets of experiments of sample preparation, storage, and spectral measurements were carried out, and several dozens FTIR spectra were collected. Fortunately, the results obtained converged nicely and hence, for the sake of brevity, we show herein only a few representative spectra. As a first stage, surface films formed on lithium in pure DOL and DOL/LiTFSI were studied. Figure 4 presents FTIR spectra measured from Li surfaces prepared in DOL and DOL/LiTFSI solutions and were kept in contact with them for 2 min. Spectra measured from Li surfaces, after being stored for days to weeks in these solutions, provided very similar information. Hence, the main surface species in these systems are formed instantaneously as the fresh active metal reaches contact with these solution species. Peak assignments for the FTIR spectra obtained in these studies are summarized in Tables I-III and also marked near some of the main IR peaks. The peak assignments are based on a couple of main sources^{30,31} and our previous work. ^{18-23,32} The v_{OH} peaks (>3300 cm⁻¹) in both spectra of Fig. 4 reflect the inevitable presence of trace water in solutions, and hence, some surface LiOH and ROH are probably formed. The spectrum related to Li-DOL reflects the formation of ROLi, HCO₂Li, and poly-DOL oligomers with -OLi edge groups (which are the sticky fingers that attach these moieties to the Li surface). The other spectrum in Fig. 4, related to Li/DOL/LiTFSI, reflects the strong impact of TFSI anion reduction in the surface films formed on lithium (relevant peak assignments appear on the spectra and in Table II). These spectral studies are in line with our previous studies which also included in situ FTIR measurements.³² The main surface reactions of Li in these DOL solutions are described in Scheme 1. The spectra of Fig. 4 demonstrate that the surface chemistry of lithium in DOL/LiTFSI solutions is dominated by reduction in the anion species to form the various possible surface species described in Scheme 1.

Figure 5 shows FTIR spectra measured from Li surfaces prepared and stored for 2 weeks in DOL, DOL/LiTFSI (0.38 M).



DOL/LiTFSI/LiNO₃ (0.31 M), and DOL/LiTFSI/LiNO₃/Li₂S₆ (0.23 M) solutions, Fig. 5a-d, respectively (see peak assignments on

the spectra in Table III). All the spectra in Fig. 5 are rich in overlapping IR peaks and bands, which makes the exact identification of

| LiTFSI (Salt spectrum for reference) | Li in DOL + PS | Li in DOL + LiNO ₃ | Li in DOL + PS + $LiNO_3$ | Peak assignments |
|--|----------------|-------------------------------|---------------------------|--|
| | 2800-3000 | 2800-3000 | 2800-3000 | νC-H |
| | 1620 | 1620 | 1620 | $\nu C = 0$ Li formate |
| | 1440–1500 | 1440–1500 | 1440–1500 | ν -CO ₂ Li carbonate and carboxilate |
| | 1300-1450 | 1300-1450 | 1300-1450 | $\delta CH, CH_2, CH_3$ |
| 330 | | | | vSSO ₂ -N |
| | | | 1350 | (sulfone amide) |
| 245 | | | Around 1200 | $\nu_{as}SO_2$ |
| 196 | 1203 | | 1230 | |
| | | | 1190 | vC-F |
| 1140 | 1153 | 1170 | 1139 | $\nu_{\rm s} {\rm SO}_2$ |
| | | | | (sulfone) |
| 1062 | 1000-1100 | 1000-1110 | 1060 | νS–O |
| | | 950 | 943 | ν S-O δ S-O bending modes |
| 795 | 800-900 | 800-900 | 800-900 | CF. C-S S-O C-(|

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Figure 5. FTIR spectra of Li surfaces (measured ex situ) from Li surfaces prepared and stored for 2 weeks in pure DOL, DOL/0.38 M LiTFSI, DOL/LiTFSI/LiNO₃(0.31 M), and DOL/0.38 M LiTFSI/LiNO₃/Li₂S₆ (0.23 M) solutions [(a)–(d), respectively]. Peak assignments appear on the spectra and in Tables I-III.

all the surface species formed on each system impossible. The spectra reflect the obvious formation of ROLi and HCO₂Li species due to DOL reduction; species containing C–F, S–O, and S==O bonds due to TFSI⁻ reduction; possible surface Li₂S and Li₂S₂ due to Li₂S₆ reduction; and possible Li_xNO_y species due to NO₃⁻ reduction. In fact, the exact identification of all these surface species is not

important for the present work. The importance of these surface studies lies in the clear trends that they reflect, as explained below.

A comparison of the FTIR spectra of Li surfaces that were in short contact with the solutions (Fig. 4) and of Li surfaces after prolonged storage (2 weeks, Fig. 5a and b) shows the pronounced sharpening of the IR peaks in the spectra related to Li surfaces after long contact with solutions. For instance, the 1600 cm⁻¹ ($v_{C=0}$) and the v_{C-H} –2700 cm⁻¹ peaks unique to HCO₂Li are pronounced in the spectrum related to Li/DOL/LiTFSI. The other v_{C-H} peaks between 2800 and 3000 cm⁻¹ related to various ROLi species become better resolved when measured from the Li surface after prolonged storage. The richness of the sharp and resolved IR peaks in the fingerprint region, $1500-700 \text{ cm}^{-1}$, reflects the fact that all the reactions in Scheme 1 and the resulting products (Li surface species) are relevant to these systems. Also various $\upsilon_{\rm OH}$ peaks in the spectra related to prolonged storage are much less pronounced, compared to those related to short contact (of Li samples in solutions), which reflects the further reduction in surface LiOH and ROH species (formed on Li due to the presence of trace water in solutions) to Li₂O and ROLi due to prolonged enough contact with Li metal. The fact that the v_{CH} peaks are sharper in spectrum Fig. 5b (DOL/LiTFSI solution) is related to the presence of Li ions in solutions that should promote all the various reduction processes by electrophilic assistance.³³ Hence, DOL reduction processes should be more pronounced in DOL/LiTFSI than in pure DOL. As seen in Fig. 5c the presence of LiNO3 in solutions has a pronounced effect on the Li surface chemistry, which is well reflected by comparing spectra Fig. 5b and c. The structure of the $\upsilon_{C\text{-}H}$ peaks changes and the IR absorption in the 1500–700 cm⁻¹ region is also intensified in spectra related to Li in LiNO3-containing solutions, compared to Li in additive-free DOL/LiTFSI solutions. LiNO3 can be reduced by Li to various insoluble LiNO_v species and Li₂O. The former species should add pronounced v_{N-O} peaks to the relevant IR spectra in the region of 1250–1000 cm⁻¹ (nitrates have their main N–O stretching bands between 1300 and 1400 cm⁻¹,³¹ the lower O/N ratio in ionic N-O compounds, so the lower is the frequency of their N-O stretching vibration⁵⁴).

LiNO3 may have another important impact: It can oxidize $Li_x SO_v$ species formed by TFSI⁻ reduction to $Li_x SO_{v+1}$, e.g., LiOS = O to $LiOSO_2$, which can be further reduced to Li_2SO_3 , etc. (see later discussion). The presence of Li_2S_6 in these solutions also pronouncedly affects the Li surface chemistry, as demonstrated in Fig. 5d. Pronounced IR bands below 700 cm^{-1} appear in spectra measured from Li surfaces after prolonged contact with DOL/LiTFSI/LiNO3/Li2S6 solutions, which relate to the S-S and Li-S bonds of the insoluble Li sulfides. When comparing the relevant spectra (e.g., Fig. 5c and d), the presence of Li_2S_6 in solutions attenuates some of the surface reactivity related to TFSI⁻ and NO₃⁻ reduction (correlates well with the relatively low impedance of Li electrodes in solutions containing Li₂S₆). However, in this work we did not develop tools for the quantitative analysis of the IR spectra thus obtained. What is presented above are samples of dozens of spectra measured, including Li stored in solutions at all possible combinations (e.g., DOL/LiTFSI/Li₂S₆, DOL-LiNO₃, DOL-Li₂S₆, DOL-LiNO₃-Li₂S₆, various concentrations, etc.). All of these spectral measurements converge to the surface chemistry described above (demonstrated by the spectral samples in Fig. 4 and 5) and presented in Scheme 1.

XPS measurements.— Highly important, complementary information was provided by XPS measurements of Li surfaces prepared and stored in solutions. Peak assignments for these studies are based on Ref. 35-42.

Figure 6 shows O_{1S} , C_{1S} , Li_{1S} , and S_{2P} spectra of Li surfaces prepared and stored for 5 h in DOL/Li₂S₆ and DOL/Li₂S₆/LiNO₃ solutions. This presentation includes the deconvolution of the broad peaks to specific peaks that reflect the various oxidation states of the elements and some relevant peak assignments. The response of N_{1S} related to both samples was close to the noise level, thereby nitrogen



Figure 6. XPS spectra of Li surfaces prepared and stored for 5 h in DOL-Li₂S₆ and DOL-Li₂S₆-LiNO₃ solutions, as indicated. C_{1S}, O_{1S}, Li_{1S}, and S_{2P} peaks are presented, including peak deconvolution and assignments.

spectra are not presented herein. As clearly seen from the attached peak assignments, these measurements are in line with the FTIR spectra and related conclusions and the scope of Li surface reactions and surface species described in Scheme 1. The difference between the O, C, Li, and S spectra of the two samples is clear and pronounced. All the spectral responses related to the presence of LiNO₃ in solution reflect an increase in the oxidation state of all the above elements. While the S_{2P} spectrum related to Li stored in a DOL/Li₂S₆ solution reflects the formation of Li₂S, and probably DOL/Li_2S_6 solution reflects the remainder L_1 Li_2S_2 on the Li surface (see deconvolution of the broad S_{2P} peak around 162-160 eV to two sharper peaks at 160 and 161.5 eV), the S_{2P} spectrum of Li prepared and stored in a DOL/Li₂S₆/LiNO₃ solution is very rich in peaks (at least 5), which reflects a variety of oxidation states of the sulfur in the surface species formed on lithium. Clearly NO₃⁻ in solutions oxidizes sulfur up to sulfate (oxidation state of 6+). The fact that NO₃⁻ in solutions acts as an oxidizer is reflected not only by the sulfur spectra (where the effect is most pronounced). In fact, comparing the O_{1S}, Li_{1S}, and C_{1S} spectra of Li surfaces prepared in these two solutions also shows that the average oxidation state of these elements is higher when Li was prepared in the LiNO₃-containing solution (compare the distributions of peaks of the highest BE related to these elements, Fig. 6).

Figure 7 presents the XPS spectra of Li samples prepared and

stored for 9 days in DOL/Li₂S₆ and in DOL/Li₂S₆/LiNO₃ solutions. The spectra of Li₁S, C₁S, N₁S, O₁S, and S₂P are compared. The spectra of Fig. 7 reflect a similar impact of the presence of LiNO₃ in solutions, as discussed above. All the spectra of the above elements show a shift of the peaks to a higher BE when the relevant solution contained LiNO₃. There are also pronounced differences between the spectra of Fig. 6 and 7 (same substrates and solutions, different storage time) due to the prolonged storage time of Li samples in solutions. These changes are important and are listed below.

1. The Li sample stored for 9 days in a solution containing LiNO₃ shows pronounced N_{1S} peaks, part of which is at relatively high BE (408 eV). Hence, the N_{1S} spectrum in Fig. 7 (LiNO₃ solution) clearly reflects the formation of Li_xNO_y surface species (e.g., LiNO₃ and LiNO₂).³⁵ Hence, the prolonged contact between Li and solution may allow a direct reaction between Li and NO₃⁻.

2. The S_{2P} spectrum of Li prepared in DOL-Li₂S₆ for 9 days contains many more peaks compared to the spectrum in Fig. 6, related to a shorter contact.

This means that prolonged storage may allow the precipitation of several insoluble species: Li_2S , Li_2S_2 , and Li_2S_3 . The presence of $LiNO_3$ in solution species leads to the formation of sulfur species of



Figure 7. C_{1S} , O_{1S} , Li_{1S} , N_{1S} , and S_{2P} XPS spectra of Li electrodes prepared and stored in DOL-Li₂S₆ and DOL-Li₂S₆-LiNO₃ solutions, as indicated. Some peak deconvolution and assignments are presented.

higher oxidation states. The peaks below 164 eV nearly disappear and a small peak presets around 168 eV (may belong to Li₂SO₄ and Li_2SO_3). 35,39,40 However the S_{2P} spectrum in Fig. 7 (prolonged storage), related to the LiNO3 solution, reflects less oxidized states compared to the parallel spectrum in Fig. 6 (short storage time). Here the impact of the reactive Li surface is demonstrated. Sufficiently prolonged storage enables further reduction in all surface species formed initially. However, we cannot expect a completed reduction in the surface species by Li because even surface species with atoms of high oxidation states can be metastable in surface films on lithium, depending on the thickness of the surface layer (and their location in the film, i.e., the distance from the surface-Li atoms). Based on the above spectral studies, we can demonstrate schematically in Fig. 8 the main effects of the various solution components on the surface chemistry of lithium. The picture in Fig. 8 explains the role of LiNO3 in solutions in preventing the shuttle mechanisms upon charging sulfur electrodes in the cells, i.e., the continuous re-

duction in $\text{Li}_2 S_n$ (n = 6,8) to $\text{Li}_2 S_m$ (m = 2,4), which prevents the final oxidation of Li_2S_n to S_8 . The passivation of Li in DOL/LiTFSI/Li2S6 solutions is not enough to avoid the continuous electron transfer from Li metal to polysulfides in solutions (through the surface films). Because several forms of polysulfides are soluble in solutions (e.g., Li_2S_6 and Li_2S_4), these electron-transfer processes do not passivate the Li electrodes. When LiNO3 is present, it is probably reduced on Li to insoluble Li_rNO_v species and oxidizes the sulfides (solution and surface species) to Li_xSO_y species that passivate the Li electrodes and thus prevent the continuous electron transfer from Li to polysulfides in solutions. The LiTFSI anion also produces Li_rSO_v species. However, in the absence of LiNO₃ (and Li_2S_n species in solutions oxidized by the nitrate species) their concentration in the surface films formed on lithium in these solutions may be too small to affect the appropriate passivation of lithium needed to avoid the electron transfer to polysulfides in solutions.

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Figure 8. A schematic presentation of the contribution of the various components in DOL/LiTFSI/Li₂S₆/LiNO₂ solutions to the surface chemistry of Li electrodes.

Conclusions

The study of the surface chemistry of highly reactive electrodes such as lithium is very problematic for the following reasons.

1. The surface chemistry of lithium in all polar aprotic solutions produces very thin surface films that passivated the active metal when reaching a certain thickness. The various surface species may contain similar functional groups and bonds. Hence, it may be difficult to achieve high resolution in the product analysis.

2. Both the Li metal and the surface films on it are highly reactive with atmospheric species. For instance, ROLi species readily react with CO₂ to form ROCO₂Li. H₂O in the atmosphere solvates all the possible surface species formed on Li and thus diffuses to the active metal through the surface films and reacts with Li to form LiOH, Li₂O, and LiH. Consequently, a special methodology had to be developed to study the surface chemistry of Li electrodes in the Li-S batteries' electrolyte solutions. Although in the past we studied very rigorously the surface chemistry of Li electrodes in a large variety of electrolyte solutions, it was necessary to go several steps further in the present study in terms of preparation of solutions, the use of a special glove box that can be evacuated and refilled with highly pure argon before each step, especially designed transfer systems, and the choice of accessories (especially for FTIR spectroscopy). The combined use of FTIR and XPS for studying the same samples is also highly important. The work presented herein is definitely state of the art in terms of the surface analysis of Li electrodes. From these studies all the possible reduction processes presented in Scheme 1 and the various functional groups appearing in the tables are indeed relevant to the surface films formed on Li in DOL/LiTFSI, Li_2S_n , and $LiNO_3$ solutions. These studies clearly showed a pronounced impact of the presence of LiNO₃ in solution on the surface chemistry of Li electrodes: Its direct reduction to form surface $Li_x NO_y$ species and the oxidation of sulfur species to form various Li_xSO_y surface moieties. This impact explains the positive effect of LiNO₃ in preventing the shuttle mechanism that avoids full charging of sulfur electrodes in Li-S cells: The enhancement of Li passivation, which remarkably diminishes the possible reduction in polysulfide species in solutions by the reactive lithium electrodes.

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