Cycling performance and surface analysis of Lithium bis(trifluoromethanesulfonyl)imide in propylene carbonate with graphite

Yue Pan^{1,2}, Guiling Wang², Brett Lucht^{1*}

¹*Department of Chemistry, University of Rhode Island, Kingston, Rhode Island 02881, United*

States

²*Key Laboratory of Superlight Materials and Surface Technology of Ministry of Education,*

College of Materials Science and Chemical Engineering, Harbin Engineering, Harbin,

150001, China

**Corresponding Author: blucht@chm.uri.edu, tel (401)874-5071, fax (401) 874-5072*

Abstract:

The performance of different concentrations of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in propylene carbonate (PC) on a binder free (BF) graphite electrode has been investigated. Variation in the salt concentration results in a change in the reduction reactions at the electrode interface and the reversible cycling of the cell. Continuous electrolyte reduction is observed at low salt concentrations while reversible lithiation/delithiation is observed at high salt concentrations. Ex-situ surface analysis of the cycled electrodes has been conducted via infrared spectroscopy with attenuated total reflectance (IR-ATR) and X-ray photoelectron spectroscopy (XPS). The ex-situ surface analysis suggests that changes in the cycling performance correlate with changes in the composition of the

solid electrolyte interface (SEI) on the surface of binder free (BF) graphite electrode.

The improved cycling performance correlates with an increase in the LiF content of the SEI.

Key words: LiTFSI; propylene carbonate; electrolyte; graphite anode.

1 Introduction:

Rechargeable Li-ion batteries (LIBs) are widely used in portable electronic devices and are rapidly being incorporated into electric vehicles due to their high volumetric and gravimetric energy density [1-6]. However, significant research activity has been directed towards the development of lithium ion batteries with greater energy density and longer calendar life. One important component of the lithium ion battery is the electrolyte [7-9]. There have been significant investigations on electrolytes for lithium ion batteries. This research has included novel salts, solvents, and additives [10-12]. One salt of significant recent interest is lithium bis(trifluorosulfonyl)imide (LiTFSI). While LiTFSI has been reported to have better thermal stability than LiPF_6 with comparable conductivity, LiTFSI has also been reported to have problems associated with corrosion of the Al current collector. Nonetheless, LiTFSI is one of the most promising alternatives to the commercial standard, LiPF_6 .

Carbonate solvents are the most frequently used polar aprotic solvents for lithium ion batteries. The electrolyte formulations typically include ethylene carbonate (EC) due to the importance of EC in the formation of the solid electrolyte interface (SEI) on graphite. However, propylene carbonate (PC) would be a preferable solvent since it has a lower melting point ($T_m = -48.8\text{ }^\circ\text{C}$) and comparable dielectric constant (65). Unfortunately, PC is continuously reduced on the graphite surface resulting in exfoliation of the graphite instead of lithium ion intercalation into the graphite [13]. However, when high concentrations of salt are used in PC the cycling performance of the cells can be significantly improved [14, 15]. The improved performance of PC

based electrolytes at high salt concentrations, is related to the recent increased interest in the performance of electrolytes with high concentrations of dissolved salt[15-21]. These investigations have highlighted the significant changes in the electrochemical performance of electrolytes at high salt concentration.

Binder free (BF) graphite electrodes have been found to be very useful for the characterization of the SEI due to the absence of binder which eliminates spectral overlap of the binder with the components of the SEI [22-24]. In this article, we report the investigation of the electrochemical properties of Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in PC as a function of salt concentration with a binder free graphite electrodes.. The electrochemical properties have been investigated via a combination of cyclic voltammetry (CV) and galvanostatic cycling. After cycling, ex-situ surface analysis of the electrodes has been investigated via a combination of Infrared Spectroscopy with attenuated total reflectance (IR-ATR) and X-ray photoelectron spectroscopy (XPS) to develop and understanding of the role of the SEI in performance.

2 Experimental:

2.1 Preparation of binder-free graphite electrodes:

Binder-free graphite electrodes were prepared via electrophoretic deposition (EPD) as previously reported [14]. The active material loading was $1.6 \sim 2.0 \text{ mg cm}^{-1}$.

2.2 Preparation of coin cells:

The experiment was carried out with CR2032 coin cells. Binder free graphite electrode is used as the working electrode, and a Li foil served as the reference and

counter electrode. LiTFSI dissolved in PC is used as the electrolyte. Six different concentrations of LiTFSI in PC were prepared (1.2, 2.2, 2.4, 2.6, 2.8, 3.2 M LiTFSI/PC), one celgard 5301 and one glass fiber have been used as the separator. The cells were assembled in an Ar-filled glove box (<1 ppm H_2O).

2.3 Electrochemical experiment:

The cycling performance was tested with a current density of C/20 ($1\text{ C}=372\text{ mA g}^{-1}$) in the potential range of 0.05-2.0 V vs. Li^+/Li by an Arbin BT2000 battery cycler at 25°C . Cyclic voltammetry (CV) was conducted using a Princeton Versa STAT 3 at 25°C with a scan rate of 0.05 mV/s in a voltage range 0.05 ~ 2.0 V. Three scans were conducted for each cell.

2.4 Infrared (IR) and X-Ray Photoelectron Spectroscopy (XPS):

IR with Attenuated Total Reflectance (ATR) and XPS were conducted on binder free graphite electrodes extracted from cycled coin cells after rinsing sequentially with the combination of DMC+PC and pure DMC, and drying over night in a vacuum. XPS and IR analysis was conducted without exposing the samples to air. Samples for XPS analysis were transferred in an air free evacuated samples holder provided by Thermo Scientific. IR-ATR was measured with a Bruker TENSOR 27 spectrometer in a nitrogen-purged glove box. The XPS was obtained on a Thermo K-Alpha system using Al $\text{K}\alpha$ radiation ($h\nu=1486.6\text{ eV}$) under ultrahigh vacuum conditions. XPS was collected at multiple locations on graphite anodes. The spectra were calibrated on the basis of the C1s graphite peak binding energy at 284.5 eV.

3 Results and discussion

3.1 Electrochemical Cycling Performance

The lithiation/delithiation curves of coin cells with electrolyte with six different concentrations of LiTFSI in PC are provided in Figure 1. The lithiation curve for the 1 M LiTFSI in PC electrolyte has a plateau at 1.0 V characteristic of the continuous reduction of PC [14, 25]. This value changes slightly to 0.85 V with 2 M LiTFSI in PC electrolyte. Interestingly upon increasing the concentration LiTFSI in PC to 2.2 M, the plateau at 0.85 V becomes a shoulder and the potential steadily decreases through stages to 0.05 V characteristic of the lithiation of graphite. The shoulder characteristic of PC reduction at ~0.85 V is lessened further when the concentration of LiTFSI is further increased. The delithiation capacities and coulombic efficiencies of the BF graphite anodes with electrolytes with six different concentrations of LiTFSI in PC are depicted in Figure 1b and listed in Table 1. The electrode cycled with 1 M LiTFSI in PC has very poor adhesion to the current collector preventing ex-situ surface analysis. It can be seen that the higher the concentration of LiTFSI, the higher the observed coulombic efficiency. The delithiation capacity of the cells cycled with 3.0 M electrolytes was 274 mAh g^{-1} , while the first cycle efficiency was ~80%. Cells with high concentrations of LiTFSI ($> 2.8 \text{ M}$), had good cycling performance for up to 20 cycles (93 % capacity retention). Similar trends in cycling performance as a function of LiTFSI concentration were observed with electrodes containing binders suggesting that the BF graphite electrodes are a good model for commercial electrodes.

Fig. 1. Lithiation/delithiation curves of the coin cells with six different concentrations of LiTFSI/PC electrolytes. (a) lithiation, (b) delithiation.

Table 1 The specific capacities and coulombic efficiencies of BF graphite anodes with electrolytes with six different concentrations of LiTFSI in PC

Concentration	2 M	2.2 M	2.4 M	2.6 M	2.8 M	3.0 M
Lithiation specific capacities	748	453	385	442	452	352

(mAh g ⁻¹)						
Delithiation specific capacities (mAh g ⁻¹)	2.70	312	283	335	340	274
Coulombic efficiencies (%)	-	68.9	73.4	75.7	75.1	77.9

Cyclic voltammetry can provide additional detail about the electrochemical reactions of the electrolyte with the electrode surface. For the electrolyte with 2.0 M LiTFSI in PC, the initial cathodic process observed on the graphite electrodes begins at ~0.8 V vs Li and results from reduction of the PC. The PC reduction peak is the only peak observed on the cathodic scan and no peaks are observed on the return anodic scan. This is consistent with continuous PC reduction and the absence of generation of a passivating solid electrolyte interface (SEI). There is no evidence for lithium ion intercalation or deintercalation from the graphite. The second and third CV curves are similar to the first except that the magnitude of the PC reduction peak is slightly diminished with each cycle. When the concentration of LiTFSI electrolyte is increased to 2.2 M, the cathodic peak characteristic of PC reduction peak is observed at ~0.75 V and an additional cathodic peak is observed at ~0.12 V characteristic of lithium intercalation into graphite. On the return anodic scan there is a single peak at ~0.22 V consistent with lithium deintercalation from graphite. Upon increasing the concentration of LiTFSI, similar CV scans are observed although the intensity of the PC reduction peak (~0.75 V) decreases slightly with increased LiTFSI concentration. The second CV scan for all of the electrolytes with high concentrations of LiTFSI (> 2.2 M) contain a single cathodic peak at ~0.12 V and a

single anodic peak at ~ 0.22 V typical for reversible lithium ion intercalation/deintercalation and reversible cycling of the cells. The changes in electrochemical performance are likely due to changes in the solution structure of the electrolyte. A previous investigation of PC in LiPF_6 suggests that upon increasing the salt concentration the species shift from solvent separated ion pairs to contact ion pairs and the different solution species lead to different reduction products. A similar change in solution structures and reduction products is likely occurring for the LiTFSI in PC electrolytes.

Fig. 2. CV curves of coin cells in six concentrations of LiTFSI/PC electrolytes cycled between 2 and 0.05 V with 0.05 mV/s.

3.2 Ex-situ surface analysis

In order to develop a better understanding of the changes occurring to the surface

of the electrodes ex-situ surface analysis of the electrodes was conducted via a combination of IR-ATR and XPS. The IR-ATR spectra of the BF-graphite electrodes fresh and cycled with electrolytes with different concentrations of LiTFSI in PC are depicted in Figure 3. The fresh electrode contains absorptions at 1350, 1200 and 1050 cm^{-1} characteristic of oxygenated impurities on the graphite surface[22]. The IR spectra of electrodes cycled with 2 M LiTFSI in PC electrolyte contain two new strong absorptions at 1490 and 1420 cm^{-1} corresponding to the presence of Li_2CO_3 [14, 26]. Upon increasing the concentration of LiTFSI to 2.2 M in PC, additional new peaks are observed at ~ 1650 and 1300 cm^{-1} are observed, which is inconsistent with the presence of lithium propylene dicarbonate[27]. Further increasing the concentration of LiTFSI results the observation of similar peaks with weaker intensity suggesting lower concentrations of PC reduction products on the surface of the BF graphite electrodes which is consistent with the first cycle efficiencies.

Fig. 3 FTIR spectrum of binder free graphite electrode and binder free graphite electrodes extracted from coin cells cycled with six concentrations of LiTFSI/PC electrolytes

The XPS spectra of binder free graphite electrodes extracted from cycled cells with six different concentrations of LiTFSI/PC electrolytes are provided in Figure 4 and the elemental concentrations are summarized in Table 2. Changes in the spectra are consistent with changes to the electrode surfaces as a result of changing the concentration of LiTFSI. As the concentration of LiTFSI is increased the concentrations of C and O are decreased, while the concentrations of F are increased (Table 2). The concentrations of N and S are low, ~1 % for total concentration of S and N combined and relatively constant.

The C1s spectrum of the fresh BF graphite electrode has a sharp peak at 284.5 eV characteristic of graphite. There is also a small broad peak in the O1s spectrum at

~532 eV consistent with the presence of some oxygenated impurities on the surface of the graphite. The XPS spectra of LiTFSI contain peaks at 293.5 eV in the C1s spectrum and at 688 eV in the F1s spectrum characteristic of $-\text{CF}_3$ from LiTFSI. In addition, there are peaks at 534 eV in the O1s, 401 eV in the N1s, and at 170 eV in the S2p characteristic of $-(\text{SO}_2)_2\text{N}-$. Upon cycling the BF graphite electrodes with the LiTFSI electrolytes similar peaks are observed for all salt concentrations, although there are some differences in the intensities of different peaks. The C1s spectrum contains new peaks at ~287 and 290 eV consistent with C–O and CO_3 in lithium alkyl carbonates and Li_2CO_3 . In addition there is a small new peak characteristic of lithiated graphite at 283.5 eV, suggesting that the SEI is relatively thin. The presence of lithium carbonates is further supported by the O1s spectrum, which contains peaks at 533.7 eV and 532 eV characteristic of C–O and C=O, respectively. The content of ROCOOLi decreases upon increasing the concentration of LiTFSI, which can be demonstrated by the decreased concentrations of C and O on the surface of BF graphite electrodes. The F1s spectrum contains new peaks at 688.5 and 684.5 eV characteristic of C–F and LiF, respectively. Interestingly, the peak characteristic of LiF increases with higher concentrations of LiTFSI, consistent with reduction of LiTFSI to generate LiF since LiTFSI is the only source of F [28,29]. The increase in LiF coincides with the decrease in the reduction peak of PC as observed by CV, consistent with a change in electrolyte reduction reaction. The presence of low concentrations of N1s and S2p suggest the presence of concentrations of other LiTFSI decomposition products on the electrode surface. The ex-situ surface analysis is

consistent with an increase in the concentration of reduction products of LiTFSI at high concentrations of LiTFSI, which likely occurs due to changes in the solution structure of the electrolyte and increased concentration of contact ion pairs making LiTFSI reduction more facile [14].

Table 2 Element percentage of rinsed binder free graphite electrodes with six concentrations of

LiTFSI/PC electrolytes.				
Atomic (%)	Li1s	C1s	O1s	F1s
Fresh		96	4	
2 M	23	42	31	3
2.2 M	23	42	31	4
2.4 M	24	41	29	5
2.6 M	28	40	25	5
2.8 M	30	39	25	6
3.0 M	28	37	25	10

Fig.4 XPS spectra of rinsed binder free graphite electrodes extracted from cycled cells with six different concentrations of LiTFSI/PC electrolytes e from top: fresh binder free graphiteelectrode, LiTFSI, 2, 2.2, 2.4, 2.6, 2.8, 3.0 M electrolytes.

4. Conclusion:

The cycling performance of binder free (BF) graphite electrodes with different concentrations of LiTFSI in PC have been investigated. At low concentration

of LiTFSI (1-2 M), the continuous reduction of electrolyte is observed at ~ 0.85 V vs Li, and no lithiation and delithiation of the graphitic anode occurs. Upon increasing the concentration above 2.2 M, a new reduction peak is observed at 0.75 V (vs. Li) by CV and reversible lithiation/delithiation of the graphite is observed. Further increases of concentrations of LiTFSI, result in increased first cycle coulombic efficiency, consistent with the improved reversible lithiation/delithiation. Ex-situ surface analysis of the cycled electrodes has been conducted via a combination of IR-ATR and XPS. The surface analysis suggests that the primary components of the SEI are Li_2CO_3 , ROCO_2Li , and LiF. Increased concentrations of LiTFSI result in decreases in the concentration of Li_2CO_3 and ROCO_2Li and increases in the concentration of LiF. These subtle changes in the composition of the SEI, in particular the increase concentration of LiF, are likely responsible for the changes in cycling performance.

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