

Short communication

# In situ micro-FTIR study of the solid–solid interface between lithium electrode and polymer electrolytes

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## Abstract

In situ micro-FTIR spectroscopy was explored to characterize the solid–solid interface between lithium electrode and polymer electrolytes. The cyclic voltammetric (CV) results indicated that the reduction reactions of oxygen and water as well as the formation of underpotential deposition (UPD) Li occur in the Li/PEO<sub>20</sub>-LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> electrolyte interface in the different potential region. The infrared spectral changes observed during the CV process revealed that there is a direct correlation between the CV peaks and the magnitude of the infrared peaks. It is shown that the infrared reflectivity from the solid–solid interface is very sensitive to the formation of the passive layer on the lithium electrodes. The results obtained from optical micrographs also displayed directly the formation of the passive layer along with lithium deposition and dissolution process. It is correlated well with in situ FTIR and electrochemical experiments.

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**Keywords:** Li electrode; Polymer electrolyte; In situ FTIR spectroscopy

## 1. Introduction

Rechargeable lithium polymer batteries using polymer electrolyte as their electrolyte have attracted a lot of attentions in recent years, due to their potential application in small portable electronic, personal communication equipment and electric vehicles (EV). They can offer a number of significant advantages both in terms of high energy density and good safety performance.

However, since Li is highly reactive towards electrolytes and impurities existing in electrolytes, such as traces of water and oxygen, a passive layer is formed on the lithium/polymer electrolytes interface. During the lithium deposition–dissolution process, undesirable morphologies of Li such as dendrites and dead Li can be formed on the Li surface. All these interfacial characteristics crucially affect the safety and cycle life of battery. Therefore, it is very important to understand and control the lithium/polymer electrolytes interface to obtain high performance lithium polymer batteries.

There have been various studies on the interfacial properties between lithium electrode and polymer electrolyte by using electrochemical techniques and ex situ spectroscopic meth-

ods [1–6]. However, fewer efforts were invested in the in situ spectroscopic study of the lithium/polymer electrolyte interface [7,8]. Unlike the liquid electrolyte systems, the polymer electrolytes are rather hard, and thus wetting and contact problems at the lithium/polymer electrolyte interface should be importantly considered. Thus, it is rather difficult to directly explore the structure and chemical composition of the interface between lithium electrode and polymer electrolyte due to lack of a proper spectroelectrochemical apparatus.

Fourier-transform infrared spectroscopy (FTIR) is recognized as a powerful technique for the in situ characterization of electrochemical systems because of its high surface sensitivity and its inherent non-destructive character. In this work, we provide a detailed description of a spectroelectrochemical cell designed in this lab and report some preliminary in situ FTIR studies of the interface between Li and a PEO-based polymer electrolyte.

## 2. Experimental

An electrochemical cell was specially designed and constructed to be compatible with our FTIR spectrometer. The cell configuration is illustrated in Fig. 1. It consists of a series of components placed adjacent to each other to form a sandwich-type thin layer cell. These include in sequence: a CaF<sub>2</sub>

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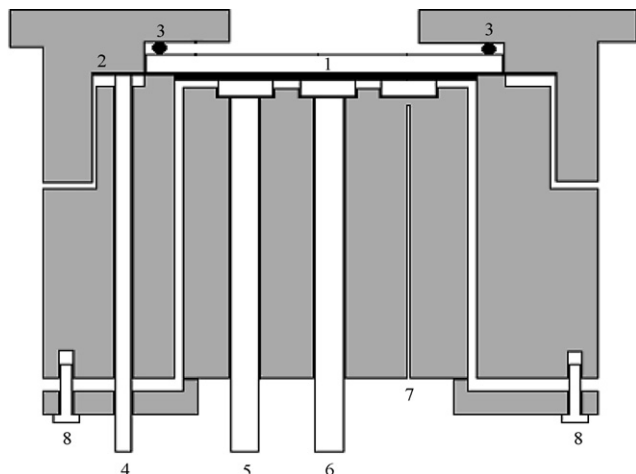


Fig. 1. Cell configuration: (1)  $\text{CaF}_2$  windows for incident and reflected IR beams; (2) copper sheet; (3) O-rings; (4) ports for working electrode; (5) ports for reference electrode, (6) ports for counter electrode; (7) thermocouple; (8) screws.

windows ( $26 \text{ mm} \times 2 \text{ mm}$ ) covered with a thin layer of gold, which is used as the semitransparent working electrode; a copper sheet as the current collector; a circular lithium disk and an annular lithium disk arranged in homocentric and coplanar style, which is used as the counter and reference electrode, respectively; the polymer electrolyte membrane positioned between working electrode and counter electrode; a thermocouple placed adjacent to the lithium piece, which can be used to monitor the temperature of the cell; O-ring and screws were used to keep the cell air-tightened.

The thickness of the gold film is a crucial factor in this cell to determine the feasibility of in situ FTIR measurements. The gold film must not only allow a significant fraction of the incident IR beam to pass through, but also provide the conductivity between the working electrode and the copper current collector. In our experiments, we optimize and obtain a proper gold film on the  $\text{CaF}_2$  windows by vacuum sputtering method. The thickness is about 30 nm (see Fig. 2). Thus, the incident IR beam can pass through the  $\text{CaF}_2$  window and the thin gold layer due to the

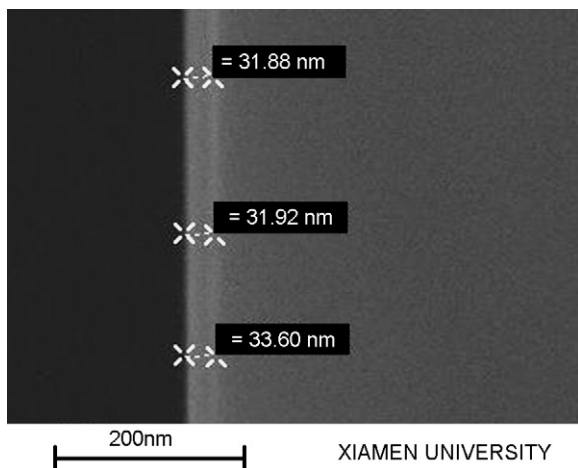


Fig. 2. SEM image of the profile of the gold film on a  $\text{CaF}_2$  window.

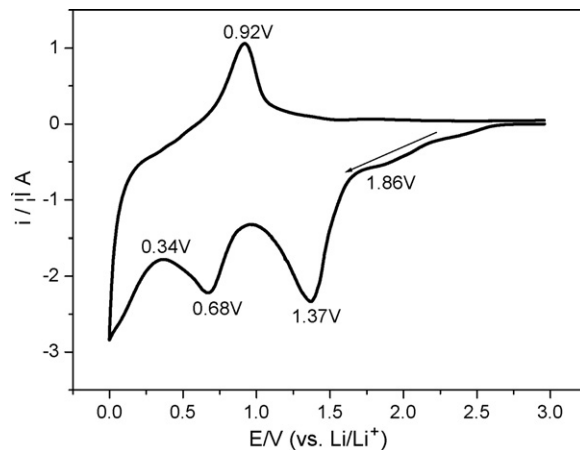


Fig. 3. The first cycle voltammogram of a gold electrode in  $\text{PEO}_{20}\text{-LiN}(\text{CF}_3\text{SO}_2)_2$  electrolyte obtained in the spectroelectrochemical cell in the range of 0–2.96 V vs.  $\text{Li/Li}^+$  at room temperature. Scan rate:  $0.5 \text{ mV s}^{-1}$ .

penetrability of the IR beam, and can be partially absorbed by species at the gold electrolyte interface.

The spectroscopic measurements were carried out on a Nicolet avatar 360 FTIR spectrometer (Thermo Nicolet Co., USA) which was equipped with a micro-reflectance accessory (Centaurus). The optical micrographs were obtained by a CCD camera assembled in the accessory using  $\mu\text{-view}$  software. The spectra were acquired in the range of  $4000\text{--}650 \text{ cm}^{-1}$  with a resolution of  $4 \text{ cm}^{-1}$  using Omnic 6.0a software. All spectra presented in this work represent the average of 32 interferometric scans. During the spectral collection, the cell was purged continuously with dry nitrogen to exclude the affect of infrared active  $\text{H}_2\text{O}$  and  $\text{CO}_2$  in the atmosphere. The hermetic effect and the degree of contact were achieved by using O-rings, grease, and screws.

Polymer electrolytes were prepared by dissolving 0.8 g of PEO powder ( $M_w = 600,000$ , Aldrich) and 0.1 g  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  salt (Aldrich) into 20 ml acetonitrile (HPLC, Shanghai Reagent). After stirring at  $50^\circ\text{C}$  for 48 h, the homogenous solution was cast into a smooth PTFE mold and evaporated with a  $4 \text{ \AA}$  molecular sieve as absorber at room temperature. Flexible polymer electrolyte membranes ( $\text{PEO}_{20}\text{-LiN}(\text{CF}_3\text{SO}_2)_2$ ) were  $\sim 80 \mu\text{m}$  thick. The Li electrode preparation and subsequent cell assembly were carried out in an Ar-filled glove box (Labmaster, Mbraun Co., Germany) with  $<1 \text{ ppm O}_2$  and  $<1 \text{ ppm H}_2\text{O}$ . Before assembling, the lithium metals were carefully scraped, in order to be clean. The hermetic effect and the degree of contact were achieved by using O-rings, grease, and screws.

The cyclic voltammetry experiment was carried out in the potential range of 0–2.96 V versus Li at a scanning rate of  $0.5 \text{ mV s}^{-1}$  by using an autolab PGSTAT30 electrochemical instrument (Metrohm Co., The Netherlands).

### 3. Results and discussion

A typical cyclic voltammogram of the gold electrode in  $\text{PEO}_{20}\text{-LiN}(\text{CF}_3\text{SO}_2)_2$  electrolyte during the first cycle obtained at room temperature in the spectroelectrochemical cell is shown

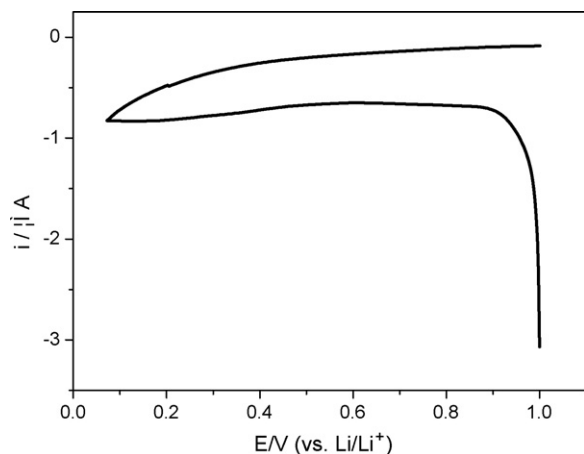


Fig. 4. Cycle voltammogram of gold electrode in  $\text{PEO}_{20}\text{-LiN}(\text{CF}_3\text{SO}_2)_2$  electrolyte obtained in the spectroelectrochemical cell in the range of 0.07–1.0 V vs.  $\text{Li/Li}^+$  at room temperature. Scan rate:  $0.5 \text{ mV s}^{-1}$ .

in Fig. 3. This curve is very similar to those obtained with other metal electrodes such as Ni and Ag under the same experimental conditions in our lab. The weak cathodic peak at around 1.86 V is ascribed to the reduction of oxygen in the electrolyte [9]. This indicates that a very thin layer possibly including lithium superoxide and lithium peroxide is formed at the Au/polymer electrolyte at this potential. The pronounced cathodic peak centered at 1.37 V is ascribed to the water reduction process [10]. The main products for the process are LiOH and  $\text{Li}_2\text{O}$  which have been proved by ex situ FTIR and Raman experiments in the literature. The larger cathodic current indicates that the layer of LiOH and  $\text{Li}_2\text{O}$  is much thicker than that formed by oxygen reduction.

The peak centered at 0.68 V in the cathodic direction may be attributed to the underpotential deposition (UPD) of Li on gold electrode. The increase in the current in the range between 0.34 and 0 V is due to the Li/Au alloy formation firstly, which is probably followed by Li bulk deposition. The unique anodic peak centered at 0.92 V is due to the stripping of the UPD Li layer [9,10].

The main emphasis of this work is focused on the interface between lithium electrode and polymer electrolyte, however, it should be noted that the above processes mostly take place at the Au/polymer electrolyte interface, we tried to build the lithium/polymer electrolyte interface by using above UPD process.

In order to further understand the character of the UPD process, we carry out the scan in the same cell in the range of 0.07–1.0 V. The cyclic voltammogram is shown in Fig. 4. However, it is particularly noted that there is little peak in the whole scan. The pronounced difference between Figs. 3 and 4 is that the UPD process of the former happened after the reduction of water and oxygen. A possible explanation for this phenomenon is that the interface between Au and polymer electrolyte may be stabilized by the layer formed by water and oxygen reduction. When the UPD process occurs, the lithium ions must probably migrate through this layer containing lithium superoxide/peroxide and LiOH/ $\text{Li}_2\text{O}$  in order to be deposited on the Au electrode. The

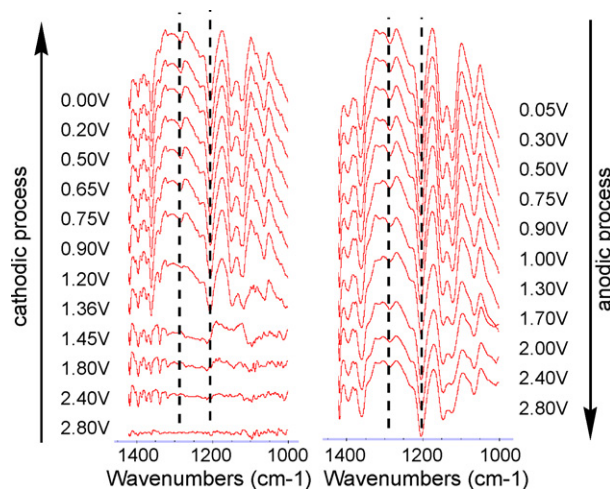


Fig. 5. Series of potential difference FTIR spectra obtained in  $\text{PEO}_{20}\text{-LiN}(\text{CF}_3\text{SO}_2)_2$  electrolyte in the spectroelectrochemical cell at room temperature during the first voltammetric cycle at  $0.5 \text{ mV s}^{-1}$  shown in Fig. 2 using as a reference the spectra recorded at 2.9 V vs.  $\text{Li/Li}^+$ .

layer may also be the direct source of the UPD Li and make the UPD process become easier. Therefore, the layer formed by the reduction of water and oxygen plays an important role for the Li UPD process in the electrode/polymer electrolytes interface.

Fig. 5 shows a series of potential difference FTIR spectra obtained in  $\text{PEO}_{20}\text{-LiN}(\text{CF}_3\text{SO}_2)_2$  electrolyte in the spectroelectrochemical cell at room temperature during the first voltammetric cycle at  $0.5 \text{ mV s}^{-1}$  (see Fig. 3). The collection of each spectrum lasted about 22 s, so the value specified in each spectrum represent the rough potential which fluctuated between +11 and –11 mV. The spectrum recorded at 2.9 V was used as a reference. These spectra display a number of both negative and positive direction peaks in the range between 1000 and  $1425 \text{ cm}^{-1}$ . Compared with the spectrum obtained at open circuit potential (see Fig. 6), all negative-pointing features are characteristic of PEO and  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ . It is known that the

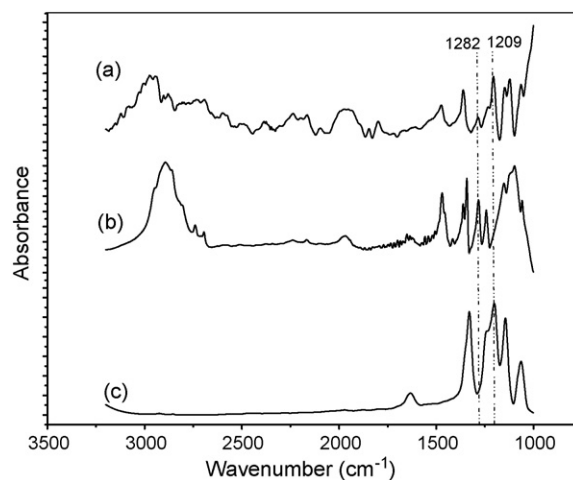


Fig. 6. FTIR spectra obtained in (a) the  $\text{PEO}_{20}\text{-LiN}(\text{CF}_3\text{SO}_2)_2$  electrolyte in the spectroelectrochemical cell at open circuit potential; (b) pure PEO; (c) pure  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ .



negative peak in this in situ FTIR spectrum implies a decrease in the amount of corresponding species probed by the IR beam. In the spectra, the negative peak at  $1282\text{ cm}^{-1}$  is assigned to  $\text{CH}_2$  twisting vibration in the PEO chain, whereas the negative peak at  $1207\text{ cm}^{-1}$  is assigned to  $\text{CF}_3$  stretching vibration in the  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  salt. The comparative result of the potential-dependent of two negative peak intensity is shown in Fig. 7.

From Fig. 7, it can be seen that the intensity of PEO and  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  both abruptly decrease at about 1.37 V in the cathodic direction, and slowly increase at about 0.92 V in the anodic direction. Linked with the cyclic voltammogram in Fig. 3, it reveals a direct correlation between the flow of charge through the electrode and the magnitude of the two peaks. This effect is most likely due to an increase or decrease in the infrared reflectivity induced by the formation of a thin layer at the Au/polymer electrolyte interface. As the potential scans to around 1.37 V in the cathodic direction, the passive layer formed by the reduction of water and oxygen leads to the decline of the peak intensity in PEO chain and  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  salt. The dissolution of UPD Li at around 0.92 V in the anodic direction may bring about the disruption of the above layer and then the peak intensity in the polymer electrolyte gradually increases. However, it is stressed that, after the UPD process occurs, there is no distinctive new peak observed from infrared spectra in the subsequent scan. This indicates that there may not be any new species formed on the interface between the UPD Li and polymer electrolyte. This conclusion is partially contradictory to the ex situ FTIR results. This is probably due to the limitation of experimental techniques such as a small angle of incidence in our experiments, infrared window ( $\text{CaF}_2$ ) and middle infrared spectrometer. In addition, because  $\text{SCN}^-$  is known to be a good probe molecular for infrared study, we have carried out the same experiment for the PEO–LiSCN system. Unfortunately, the results from the PEO–LiSCN system is not satisfied at present due to the complexing action between Au electrode and  $\text{SCN}^-$  ion.

Such a change in the formation and disruption of the passive layer can be also directly observed by the optical micrographs obtained from the micro-FTIR spectrometer. Fig. 8 presents a

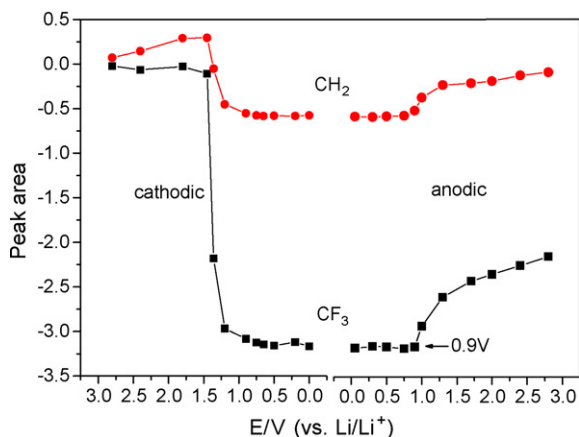


Fig. 7. A comparison of potential-dependent of peak intensity between  $\nu_{\text{CH}_2}$  in the PEO chain and  $\nu_{\text{CF}_3}$  in the  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  salt.

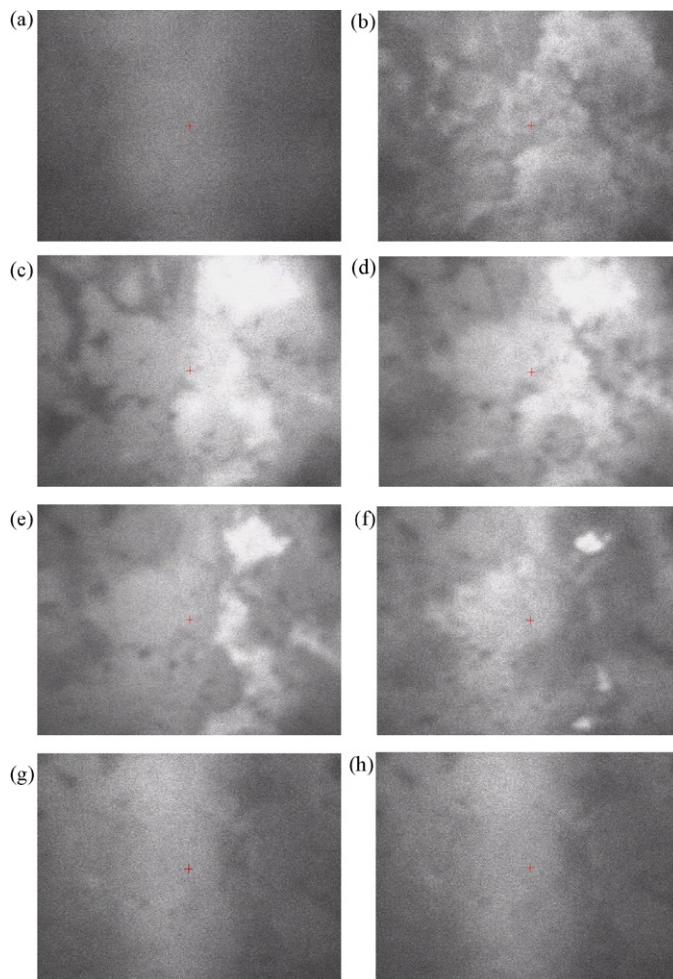


Fig. 8. Optical micrographs ( $450\ \mu\text{m} \times 340\ \mu\text{m}$ ) on the Au electrode at different scan potential during the first voltammetric cycle shown in Fig. 2. (a)  $-2.5\ \text{V}$ ; (b)  $-1.36\ \text{V}$ ; (c)  $-0.65\ \text{V}$ ; (d)  $-0.0\ \text{V}$ ; (e)  $+0.65\ \text{V}$ ; (f)  $+0.90\ \text{V}$ ; (g)  $+1.4\ \text{V}$ ; (h)  $+2.5\ \text{V}$  (vs. Li).

series of optical micrographs at different scan potential in the spectroelectrochemical cell during the first voltammetric cycle (see Fig. 3). The infrared spectra were acquired at the red cross which was hit by the IR beam. As the potential is scanned in the cathodic direction, the micrograph at 1.36 V (see Fig. 8(b)) indicates the formation of the thin layer due to the reduction of oxygen and water, whereas half of the micrograph at 0.65 V (see Fig. 8(c)) become luminant due to the formation of the UPD Li. However, as the potential moves to more anodic direction, the bright area is becoming more and more weak and disappears finally (see Fig. 8(e)–(h)).

#### 4. Conclusion

In this work, we design and optimize a proper in situ FTIR spectroelectrochemical apparatus, and thus demonstrate its feasibility for the study of the interface between Li and  $\text{PEO}_{20}\text{-LiN}(\text{CF}_3\text{SO}_2)_2$  electrolyte. The results from CV curve indicates that the formation of the passive layer (mainly containing Li oxides) by water and oxygen reduction can stabilize

the Au/polymer electrolyte interface and make the Li UPD process become easier. The changes observed from the infrared spectra and optical micrographs during the whole CV scan show clearly that there is a direct correlation between the CV peaks and the magnitude of the infrared peaks or the morphology of the interface. It is shown that the formation of a thin layer in the interface has great effects on the infrared reflectivity from the interface studied. If we want to get detailed molecular vibrational information from Li/polymer electrolytes, it still needs some improvements in the apparatus.

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