



ELSEVIER

Journal of Power Sources 97–98 (2001) 624–627

JOURNAL OF  
**POWER  
SOURCES**

www.elsevier.com/locate/jpowsour

# The effects of chemical composition of adsorbed molecular layers on lithium electrode/polymer electrolyte interface stabilization

Maryline Le Granvalet-Mancini<sup>a</sup>, Dale Teeters<sup>b,\*</sup><sup>a</sup>Laboratoire de Chimie des Solides, Institut des Matériaux de Nantes, Université de Nantes, UMR CNRS No. 6502, B.P. 329, 44322 Nantes Cedex 3, France<sup>b</sup>Department of Chemistry and Biochemistry, The University of Tulsa, 600 S. College Ave, Tulsa, OK 74104-3189, USA

Received 6 June 2000; accepted 4 December 2000

## Abstract

Previous work in our laboratory has shown that the adsorption of self-assembled molecular layers on a polymer electrolyte surface can make the interface between the electrolyte and a lithium metal electrode more stable and can hinder the growth of the type of passivation layer that inhibits ion movement between the electrode and electrolyte. This work is concerned with the effect that the molecular composition of the adsorbed layer has on interface stability. Several compounds of the form R-(CH<sub>2</sub>CH<sub>2</sub>O)-H have been found to adsorb on the surface of the polymer electrolyte and stabilize the interface. It was found that the R group could be a long, straight hydrocarbon tail capable of forming an ordered self-assembled structure or a branched hydrocarbon or a siloxane with bulky hydrocarbon groups that form a brush-type structure. Molecules of the form R-OH and R-COOH, where R was a long, straight-chain hydrocarbon, would adsorb but appeared to have much disorder in their hydrocarbon chains. It is proposed that this disorder results from a low adsorption density that results in regions where the lithium metal can come in direct contact with the polymer electrolyte causing reactions that promote interface destabilization. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Lithium electrode/polymer electrolyte interface; Lithium passivation layer; Self-assembled molecular layers; Interface stabilization

## 1. Introduction

Lithium metal/polymer electrolyte batteries have several potential advantages, including high energy density and a large electrochemical window. One potential problem with all lithium metal-based batteries is the formation of a non-stable passivation layer at the lithium/polymer electrolyte interface which can grow to have a higher resistance than the bulk electrolyte itself. While solid polymer electrolyte systems do help to stabilize the lithium metal/electrolyte interface, this interfacial problem still exists. This problem must be solved for lithium metal batteries to reach their potential in commercial utilization. Because of this problem, the electrochemistry at the electrode/electrolyte interface has been the object of several studies.

Many of the previous studies on lithium or lithium alloy anodes in contact with polymer electrolytes have involved complex impedance spectroscopy or other electrochemical techniques [1–14]. Fauteux [4] has attributed a low frequency semicircle in Nyquist plots to interfacial resistance due to a reactive film that forms at the surface of the Li

electrodes. Bruce and Krok have shown the importance of interfacial impedance in lithium/polymer electrolyte system. Their work has shown that with time the non-stable interface can increase in resistance until it is significantly larger than the bulk resistance, which would have detrimental effects on battery performance [3,11]. Sequeira and Hooper [6] and Xu and Farrington [7] have studied the kinetics of the charge transfer process at this interface and Thevenin and Muller [9] and Munichandraiah et al. [10] have examined and reviewed models based on reactions occurring at the lithium/polymer electrolyte interface. Because of the importance of this interface, various studies dealing with the stabilization of the lithium/electrolyte contact area have been conducted. Some researchers have approached this problem by studying and modifying the lithium metal surface [11–15]. However, the polymer electrolyte surface is a much easier surface with which to work than the extremely reactive lithium surface. Scrosati and coworkers have shown that the addition of inert, ceramic fillers, such as Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> will stabilize the interface [16,17]. Recent studies conducted in our laboratory [18–20] have shown that self-assembled molecular layers placed on the polymer surface can offer protection from passivation and stabilize the interface. AC impedance spectroscopy has shown that molecules

\* Corresponding author. Tel.: +1-918-6313147; fax: +1-918-6313404.  
E-mail address: dale-teeters@utulsa.edu (D. Teeters).

of the form  $\text{H}-(\text{CH}_2)_m-(\text{CH}_2-\text{CH}_2-\text{O})_n-\text{H}$  adsorbed on PEO electrolyte surfaces and stabilized the lithium/polymer electrolyte interface in lithium symmetric cells stored under an open-circuit potential [18,19]. It appears that the poly(ethylene oxide)-like portion of these molecules preferentially orient to adsorb onto the poly(ethylene oxide) electrolyte film. This leaves the  $\text{CH}_2$  segment of the molecule to self-assemble into an ordered layer just above the electrolyte surface. Studies show that this hydrocarbon layer, which now comes in contact with the lithium instead of the polymer electrolyte, is not reactive with the metal and therefore stabilizes the interface by forming a new type of solid electrolyte interphase (SEI) [19,20]. Movement of ions through this hydrocarbon layer is only slightly lowered, due most likely to the ions' ability to move through defects in the layer [19].

This work is concerned with how changing the chemistry of the adsorbed molecules affects the ability of the molecules to adsorb and to stabilize the lithium/polymer electrolyte interface.

## 2. Experimental

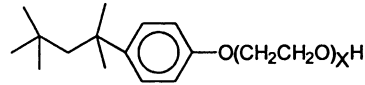
All polymer electrolyte films were made by using poly(ethylene oxide) and lithium triflate (both from Aldrich) with a 15:1 ratio of ether oxygen to lithium. Films were prepared in an argon atmosphere and were dried and stored at  $50^\circ\text{C}$  in a vacuum oven. Previous work used semicrystalline waxes having the general form  $\text{H}-(\text{CH}_2)_m-(\text{CH}_2-\text{CH}_2-\text{O})_n-\text{H}$  as the molecules for adsorption on the polymer electrolyte surface [19]. For this work, other molecules that might adsorb on the polymer surface were used. A long, straight-chain alcohol and a long, straight-chain carboxylic acid from Petrolite Specialty Polymers, two siloxane surfactants from Dow Corning, and the surfactant Triton X100 from Acros Chemicals were studied. Formation of adsorbed layers was accomplished via adsorption from a hexane solution. The complete procedure for film preparation and formation of the self-assembled molecular layers on the film has been described previously [18,19]. Surface infrared spectra, using the ATR technique, were collected on a Nicolet 510P fourier transform infrared spectrometer with a DTGS detector at  $1\text{ cm}^{-1}$  spectral resolution. The average depth of penetration of the infrared radiation into the surface can be calculated [19] and was found to be ca.  $1.0\ \mu\text{m}$ . An HP 4194-A ac impedance/gain phase analyzer was used to investigate the electrochemistry of symmetric lithium cells. This was done over a range of 40 MHz to 10 kHz. Test cells for impedance analysis were assembled in a glove box under argon and ac impedance tests were done at  $50^\circ\text{C}$  under vacuum.

## 3. Results and discussion

The molecules used in adsorption studies in this investigation and, for comparison, those used in previous

Table 1

Compounds used in adsorption studies and their ability to stabilize the lithium/polymer electrolyte interface

Chemical formula	Ability to stabilize lithium/polymer interface
$\text{H}(\text{CH}_2)_{32}(\text{CH}_2\text{CH}_2\text{O})_3\text{H}$	Yes <sup>a</sup>
$\text{H}(\text{CH}_2)_{32}(\text{CH}_2\text{CH}_2\text{O})_{10}\text{H}$	Yes <sup>a</sup>
$\text{H}(\text{CH}_2)_{40}(\text{CH}_2\text{CH}_2\text{O})_3\text{H}$	Yes <sup>a</sup>
$\text{H}(\text{CH}_2)_{40}(\text{CH}_2\text{CH}_2\text{O})_{13}\text{H}$	Yes <sup>a</sup>
$\text{H}(\text{CH}_2)_{50}\text{OH}$	No
$\text{H}(\text{CH}_2)_{77}-\text{C}(=\text{O})-\text{OH}$	No
$\text{HO}-(\text{CH}_2\text{CH}_2\text{O})_{12}-\text{Si}(\text{CH}_3)_2-\text{O}-(\text{CH}_2\text{CH}_2\text{O})_{15}-\text{Si}(\text{CH}_3)_2-\text{H}$	Yes
$\text{CH}_3-\text{Si}(\text{CH}_3)_2-\text{O}-\text{Si}(\text{CH}_3)_2-\text{O}-\text{Si}(\text{CH}_3)_2-\text{O}-\text{C}_3\text{H}_6\text{O}-(\text{CH}_2\text{CH}_2\text{O})_{12}-\text{H}$	Yes
	Yes

where X = 9-10

<sup>a</sup> Previous work [19].

adsorption work, are given in Table 1. The presence of the adsorbed molecular layers was determined by ATR-FTIR spectroscopy in the same manner as reported previously [18,19]. All molecules investigated in this work adsorbed on the PEO polymer electrolyte surface.

AC impedance data for lithium symmetric cells were collected at various times to a maximum time of ca. 160 h PEO electrolyte films and PEO electrolyte films with the molecules listed in Table 1 adsorbed on the surface were studied. Nyquist plots of these data are shown in Figs. 1 and 2, where the frequency is decreasing from left to right. The data shown in Fig. 1 are for a poly(ethylene oxide) film with no adsorbed molecular layer, for a film with the  $\text{H}-(\text{CH}_2)_{50}-\text{OH}$  molecule adsorbed onto its surface and the  $\text{H}-(\text{CH}_2)_{77}-\text{COOH}$  adsorbed film. These data show two overlapping semicircles present in the lithium symmetric cells at open circuit voltage. The capacitance of these semicircles was estimated by knowing that the maximum of each semicircle should obey the relation:  $\omega RC = 1$ . The first semicircle has a capacitance in the range of picofarads, usually associated with the bulk response, while the second has a value in the range of  $10^{-8}$  F, indicating the response of a passivating film at the Li/polymer electrolyte interface [21]. Fig. 2 shows ac impedance data for the Triton X100 and the two siloxane surfactants. The molecular layers formed by these three surfactants appear to prevent the formation of an ever-increasing second semicircle associated with the passivation layer due to a non-stable interface.

Before discussing the ability of the adsorbed layers to stabilize the interface, one interesting trend seen for the

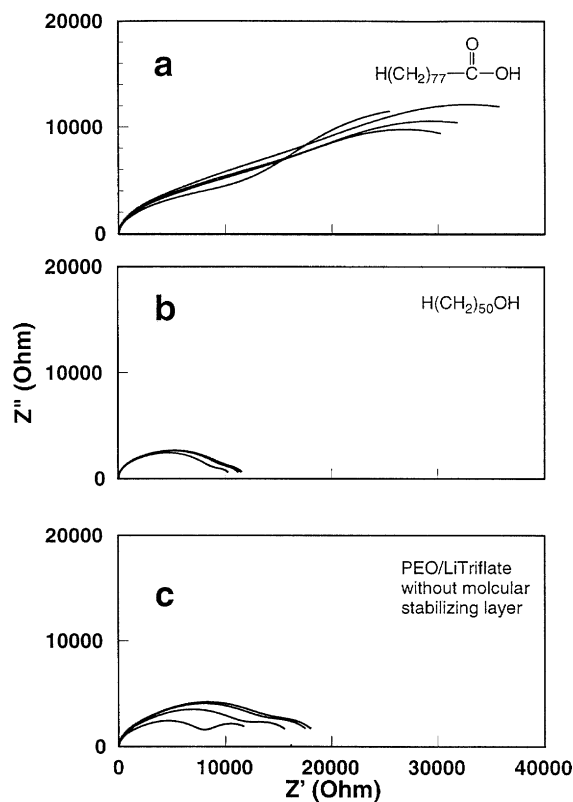


Fig. 1. Nyquist plots for symmetric lithium cells: plots (a) and (b) are for the acid and alcohol adsorbed on the PEO electrolyte film. Plot (c) is the PEO film with no adsorbed molecules. A second semicircle is seen in the plots indicative of a non-stable interface. Thickness of the polymer electrolyte films ranged between 60 and 80  $\mu\text{m}$  with a surface area of 1.58  $\text{cm}^2$ .

resistance of the bulk electrolyte (first, high frequency semicircle) should be discussed. With time the resistance is seen to increase slightly for the bulk. Previous work has attributed this behavior to change in the crystalline nature of the bulk PEO [19].

Table 1 also presents data as to whether or not the listed molecular films will prevent passivation, thus stabilizing the lithium/polymer electrolyte interface. This will be helpful in discussion of the present work. All molecules having a  $-(\text{CH}_2\text{CH}_2\text{O})-$  tail are able to stabilize the interface. Only the adsorbed alcohol and the carboxylic acid are not able to perform this function. Since past work was done on ordered hydrocarbon chains that stabilized the interface [19], an ATR-FTIR investigation of  $\text{CH}_2$  chain order was done for the alcohol and the carboxylic acid used in this study. Fig. 3 shows IR data for the  $\text{CH}_2$  stretching region for the alcohol and acid adsorbed on the surface (top spectrum in Fig. 3a and b) and for the pure compounds, which are solid, semi-crystalline, waxy materials (bottom spectra Fig. 3a and b). The antisymmetric and symmetric  $\text{CH}_2$  stretching modes in the pure compounds are seen at frequencies of 2915 and 2847  $\text{cm}^{-1}$ , respectively. These are indicative of well-ordered, crystalline hydrocarbon tails [22] and would be expected in these semi-crystalline solids. In our previous work [19], vibrational modes of approximately the same

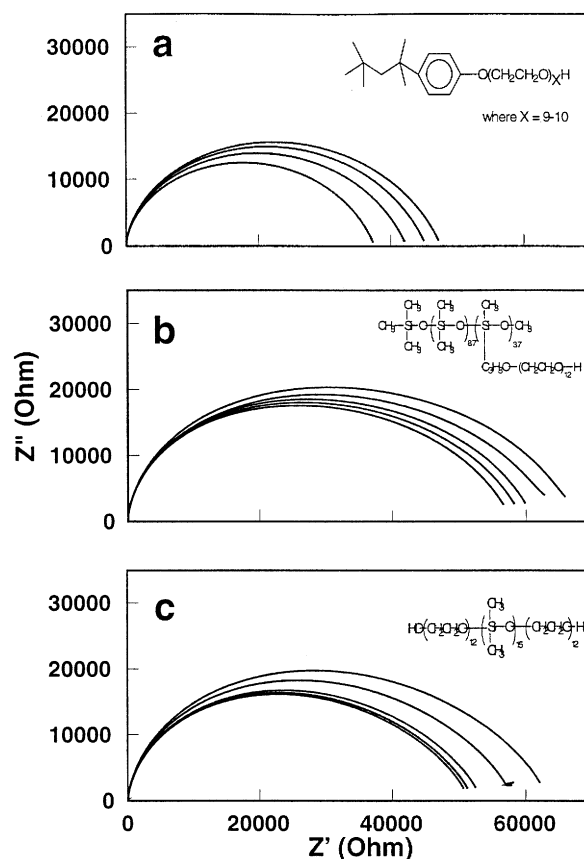


Fig. 2. Nyquist plots for symmetric lithium cells: plots (a), (b), and (c) are for the Triton X100, and the two Dow Corning siloxane surfactant, respectively. No second semicircle is observed indicating a stable interface. Thickness of the polymer electrolyte films ranged between 60 and 80  $\mu\text{m}$  with a surface area of 1.58  $\text{cm}^2$ .

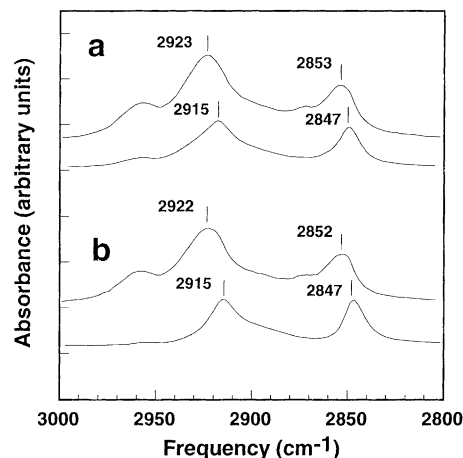


Fig. 3. ATR-FTIR spectra of  $\text{CH}_2$  stretching region for (a) the acid and (b) the alcohol. The bottom spectrum in each set is of the pure, semicrystalline solid wax. The top spectrum is of the respective compounds adsorbed on a PEO polymer electrolyte surface. The shift to higher frequency for the adsorbed molecules indicates more disorder.

frequency have been seen for molecules adsorbed on the polymer surface. This is indicative of the ordered, self-assembled hydrocarbon tail that certainly could be one condition necessary for interface stabilization. However, the top spectra in Fig. 3a and b for the adsorbed alcohol and acid show that the antisymmetric and symmetric stretching modes have increased in frequency from 5 to 8  $\text{cm}^{-1}$ . An increase in frequency to this degree has been attributed to disorder in the hydrocarbon chains due to more gauche conformations [23].

Knowing that the alcohol and acid are adsorbed on the surface and that the hydrocarbon tails of such molecules would tend to self-assemble, a reason for their apparent disorder is necessary to understand these systems. A possible explanation for this lack of order could be in the adsorption density. It is known from previous work [18,19] and this current study that molecules with  $-(\text{CH}_2\text{CH}_2\text{O})_m-$  tails readily adsorb and form what seem to be continuous self-assembled hydrocarbon surfaces. These tails must adsorb to the surface by intermingling tightly or adsorbing closely with surface PEO polymer electrolyte molecules. This results in the hydrocarbon portion of the molecule's ability to self-assemble in an ordered layer. Here it seems that the alcohol and the acid are able to adsorb on the surface, but perhaps to only certain polar regions where an ether oxygen is exposed on the polymer electrolyte surface. These adsorption sites may be too far apart for the hydrocarbon tails to self-assemble properly, resulting in the disordered chains shown by the IR spectra. Indeed, areas may exist where the adsorbed molecules are so far apart that the lithium can easily "see" the polymer electrolyte surface, resulting in reactions occurring that are responsible for interface destabilization. Interestingly, it is hard to imagine that the Triton X100 and the siloxane surfactants would form an ordered structure on the surface because of the branching and bulky pendant groups on these molecules. One would expect what is commonly called a "brush" surface that has little order to be the surface structure of preference. However, having the  $-(\text{CH}_2\text{CH}_2\text{O})_m-$  tails adsorb densely on the polymer electrolyte surface results in the brushes being very closely packed, albeit disordered, presenting a continuous protective surface that the lithium experiences. These interfaces are thus also stabilized.

#### 4. Conclusions

Molecules having the general form  $\text{R}-(\text{CH}_2\text{CH}_2\text{O})_m-\text{H}$  can adsorb on PEO polymer electrolyte surfaces. Adsorption of these molecules stabilizes the lithium/polymer electrolyte interface, whether the R group is a long, straight hydrocarbon tail capable of forming an ordered self-assembled structure or a branched hydrocarbon or a siloxane with bulky hydrocarbon groups that form a brush structure. The critical factor appears to be that the R group forms a continuous layer that does not allow the lithium to "see" the polymer

electrolyte surface thus preventing reactions from occurring that can destabilize the interface. While molecules of the type  $\text{R}-\text{OH}$  and an  $\text{R}-\text{COOH}$ , where R was a long, straight-chain hydrocarbon, were found to adsorb on the surface, they did not stabilize the interface. This was attributed to a low adsorption density resulting in the inability of the R groups to form a continuous protective molecular layer. These adsorbed molecular protective layers placed on "dry" polymer electrolytes, as studied here, or on gel polymer electrolyte systems have the potential to stabilize both the anode and cathode interfaces. Future work will investigate the use of this technique for interface stabilization using various anode materials, such as graphites and different cathode systems.

#### Acknowledgements

The authors would like to acknowledge funding from the NSF EPSCoR through Grant OSR-9550478 and the DEPS-CoR program of the Air Force Office of Scientific Research.

#### References

- [1] P.R. Sorensen, T. Jacobsen, *Electrochim. Acta* 17 (1982) 1671.
- [2] B.C.H. Steele, G.E. Lagos, P.C. Spurdens, C. Forsyth, A.D. Ford, *Solid State Ionics* 10 (1983) 391.
- [3] P.G. Bruce, F. Krok, *Solid State Ionics* 36 (1989) 171.
- [4] D. Fauteux, *Solid State Ionics* 17 (1985) 133.
- [5] M. Hiratani, K. Miyauchi, T. Kudo, *Solid State Ionics* 28-30 (1988) 1431.
- [6] C.A.C. Sequeria, A. Hooper, *Solid State Ionics* 9/10 (1983) 1131.
- [7] J. Xu, G.C. Farrington, *Solid State Ionics* 74 (1994) 125.
- [8] N. Munichandraiah, L.G. Scanlon, R.A. Marsh, B. Kumar, A.K. Sircar, *J. Electroanal. Chem.* 379 (1994) 495.
- [9] J.G. Thevenin, R.H. Muller, *J. Electrochem. Soc.* 134 (1987) 273.
- [10] N. Munichandraiah, L.G. Scanlon, R.A. Marsh, *J. Power Sources* 72 (1998) 203.
- [11] P.G. Bruce, F. Krok, *Electrochim. Acta* 33 (1988) 1669.
- [12] J.L. Goldman, R.M. Mank, J.H. Young, V.R. Koch, *J. Electrochem. Soc.* 127 (1980) 1461.
- [13] V.R. Koch, J.L. Goldman, C.J. Mattos, M. Mulvaney, *J. Electrochem. Soc.* 129 (1982) 1.
- [14] K.M. Abraham, J.S. Foos, G.L. Goldman, *J. Electrochem. Soc.* 131 (1984) 2197.
- [15] Z.I. Takehara, Z. Ogumi, K. Kanamura, Y. Uchimoto, in: *Proceedings of the Symposium on Lithium Batteries*, Vol. 94-4, The Electrochemical Society, Pennington, NJ, 1994, p. 13.
- [16] G.B. Appetecchi, F. Croce, L. Persi, F. Ronci, B. Scrosati, *Electrochim. Acta* 45 (2000) 1481.
- [17] F. Croce, R. Curini, A. Martinelli, L. Persi, F. Ronci, B. Scrosati, R. Caminiti, *J. Phys. Chem. B* 103 (1999) 10632.
- [18] R.N. Mason, M. Smith, T. Andrews, D. Teeters, *Solid State Ionics* 118 (1999) 129.
- [19] M. Le Granvalet-Mancini, L. Honeycutt, D. Teeters, *Electrochim. Acta* 45 (2000) 1491.
- [20] M. Le Granvalet-Mancini, T. Hanrath, D. Teeters, *Solid State Ionics* 135 (2000) 283.
- [21] P.G. Bruce, in: J.R. MacCallum, C.A. Vincent (Eds.), *Polymer Electrolyte Reviews*, Vol. 1, Elsevier, London, 1987, p. 237.
- [22] F. Bensebas, T.H. Ellis, E. Kruus, R. Voicu, Y. Zhou, *Langmuir* 14 (1998) 6579.
- [23] R.G. Snyder, H.L. Strauss, C.A. Elliger, *J. Phys. Chem.* 86 (1982) 5145.