



# Spectroscopy study of ionic liquid restructuring at lead interface



Ove Oll, Tavo Romann\*, Piret Pikma, Enn Lust

Institute of Chemistry, University of Tartu, Ravila 14A, 50411 Tartu, Estonia

## ARTICLE INFO

### Article history:

Received 4 December 2015  
Received in revised form 7 August 2016  
Accepted 8 August 2016  
Available online 9 August 2016

### Keywords:

Lead film  
EMImBF<sub>4</sub>  
Differential capacitance  
SEIRA  
Electrical double layer structure  
Ultra-high vacuum dried ionic liquid

## ABSTRACT

Cyclic voltammetry, electrochemical impedance spectroscopy and surface enhanced infrared absorption (SEIRA) spectroscopy have been applied for the study of the electrical double layer of the magnetron sputtered thin film Pb|1-ethyl-3-methylimidazolium tetrafluoroborate room-temperature ionic liquid system. A wide potential range of ideal polarizability has been established for the system between  $-1.6$  and  $-0.1$  V vs. Ag|AgCl in the same ionic liquid, in which the differential capacitance-potential curve is shown to have two maxima with a minimum at the perceived potential of zero charge. The first application of the in situ SEIRA technique for the study of Pb electrodes in an electrolyte solution is shown and the results are put into context of the latest developments concerning screening of metal interfaces in ionic liquid medium. Slow kinetics of oxide reduction reaction is demonstrated, which may limit the application of dry ionic liquids in lead-acid batteries.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Lead is a p metal that is mostly known for its toxicity; nevertheless it is also widely used in many different technological applications [1–3], of particular note being the lead-acid battery [4]. Also of interest is the potential use of ionic liquids (ILs) in lead-acid batteries [5] and for the electrodeposition of Pb [6–8]. However, for both of the applications and for many others [9–12], a fundamental understanding of the metal|room-temperature ionic liquid electrical double layer (EDL) structure is of vital importance. It is thus the main scope of this article to provide fundamental data for Pb|IL interface and an attempt to derive a better understanding of the interfacial structure.

In situ surface enhanced infrared absorption (SEIRA) spectroscopy is a powerful analytical tool developed by Osawa et al. [13,14] that provides strongly enhanced and surface specific information of metal interfaces. Similarly to its bigger ‘brother’, surface enhanced Raman spectroscopy (SERS), the use of SEIRA has been extended from the conventional coinage metals [13–15] to platinum group metals [15] as well as more exotic metals like Sn [16], Co [17], Ni [15], Cd [15,18], and Bi in our own works [19,20]. However, neither in situ SERS nor SEIRA spectra of Pb are reported in the scientific literature. On the contrary, underpotential deposition of Pb on Ag surfaces is seen to quench the SERS signal of the substrate [21]. To our knowledge, only one article has been published that show the SEIRA technique being applied to Pb metal surfaces [22]. Yoshidome et al. showed infrared enhancement of *p*-nitrobenzoic acid layer on a 53 nm thick thermally evaporated Pb film, whereas infrared bands became bipolar for a 95 nm Pb film.

There is also one paper, where infrared spectra of dithiol or thiolate whiskers on a Pb film have been measured, although surface enhancement effect was not proved [23]. Nevertheless, as the interfacial processes at Pb electrodes are of scientific importance, an attempt is made to measure both in situ SEIRA and SERS of thin film Pb electrodes in IL media.

## 2. Experimental

Pb was deposited using UHV AJA International magnetron sputtering system: base vacuum  $10^{-9}$  Torr, 3 mTorr Ar pressure, 25 W RF source, 2" Pb (99.995%) target. The film deposition rate  $1 \text{ \AA s}^{-1}$  was controlled using a quartz crystal microbalance. Atomic force microscopy (AFM) data were obtained by Agilent Technologies Series 5500 system, in dry air conditions. The AFM data has been analyzed using the Gwyddion software [24]. The infrared spectroscopic measurements were performed using a PerkinElmer Spectrum GX FTIR equipped with a liquid nitrogen-cooled mid-range MCT detector and Raman spectra were taken with Renishaw inVia microRaman, using 457, 633 and 785 nm laser excitation lines. Electrochemical measurements were conducted using an Autolab PGSTAT 30 potentiostat in a three-electrode glass cell with an Ag|AgCl wire in the same IL for a pseudo-reference electrode ( $-0.19$  V vs. ferrocene/ferrocenium couple measured on Pt, glassy carbon and carbon fiber electrodes). Potential cycling rates between  $10$  and  $100 \text{ mV s}^{-1}$  were applied and impedance spectra measured within ac frequency range from  $10^{-2}$  to  $10^5$  Hz with 5 mV ac modulation amplitude. 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMImBF<sub>4</sub>) from Solvionic (99.5%, H<sub>2</sub>O ~ 100 ppm) was additionally dried in ultra-high vacuum (UHV) at 90 °C for 48 h, until

\* Corresponding author.

E-mail address: [tavo.romann@ut.ee](mailto:tavo.romann@ut.ee) (T. Romann).

reaching a pressure of  $5 \times 10^{-9}$  Torr and water content below the detection limit of Karl-Fischer method ( $<5$  ppm).

Our constructed spectroelectrochemical system [25] uses deposited Pb film on the flat side of a 10 mm diameter infrared transparent Si ( $n = 3.4$ ) hemisphere as the working electrode. The small glass cell also includes a Pt spiral as a counter electrode and Luggin capillary for the connection of the reference electrode.  $0.4 \text{ cm}^3$  EMImBF<sub>4</sub> was added to the dried cell inside an argon filled glove box; thereafter the cell was sealed with PTFE stoppers. Infrared (IR) beam was directed through a ZnSe wire grid polarizer (Pike Technologies) and a ZnSe lens to the attenuated total reflectance (ATR) hemisphere at 65 degrees of incidence.

IR measurements were carried out in an inert atmosphere at temperature of 23 °C. Spectra in the potential ( $E$ ) region of  $-1.8 \text{ V} < E < -0.1 \text{ V}$  were measured relative to the reference potential of  $-1 \text{ V}$  (this potential has been selected as it is later interpreted to be the pzc). Measurements started from  $-1.0 \text{ V}$  to the more negative potential direction. 128 scans at a resolution of  $4 \text{ cm}^{-1}$  were collected at each fixed potential and the measurement cycle was repeated 3 times (and was later averaged). The resulting spectra were calculated by dividing the sample spectrum measured with the reference spectrum and presented as absorbance  $A$ , so that the positive-going bands represent an increase of a particular species at the sample potential relative to that at the reference potential. The measured bands were assigned to certain vibrations with the help of DFT-B3LYP calculations with 6-311++g\*\* basis set applying GAMESS software [26]. Initial ion-pair geometries were taken from the literature [27]. Polarizable continuum model (PCM) was applied in order to obtain a better fit to the experimental spectra. Solvent parameters for the PCM method were extracted from literature [28,29].

### 3. Results and discussion

#### 3.1. AFM measurements and film characterization

The Pb film with an average thickness of 50 nm (Fig. 1) consists of small, rather uniform crystals with an average grain size of 117 nm and has a root-mean-square roughness (rms) of 19.2 nm. On the 100 nm thick Pb film (not shown) the crystals have grown during the deposition into larger sinuously shaped particles with an average grain size of 177 nm and rms of 26.5 nm. The surface roughness factors of 1.21 and 1.19 have been established for the 50 and 100 nm thin films, respectively. The films are seen as polycrystalline in nature. AFM data in

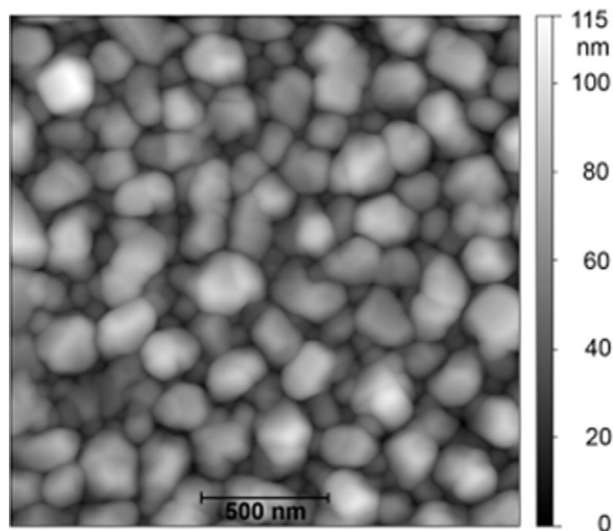


Fig. 1. AFM image of magnetron sputtered Pb thin film (50 nm mass thickness) on a glass slide.

Fig. 1 is also well characterizing the surface structure of Pb films deposited on Si hemisphere used for the SEIRA measurements. Due to the relatively low melting point of Pb (327 °C) the deposited films are significantly rougher with higher average grain size compared to those of coinage metals. Because of the high surface roughness, films below 50 nm mass thickness have resistance over  $M\Omega$ , thus being composed of separated nanoparticle islands. The 100 nm thick Pb film has been applied for the electrochemical experiments in order to ensure metallic character and homogeneity of the surface while 50 nm films have been applied for the SEIRA measurements in order to limit light absorption in the metal phase.

#### 3.2. Surface handling conditions

As is characteristic to most p block metals, the deposited Pb films are readily, even when handled only in inert gas conditions with trace amounts of O<sub>2</sub> and H<sub>2</sub>O, covered with a surface oxide layer that prevents further corrosion of the Pb electrode surface. In our system, a thin oxide layer is likely formed during contact of trace oxygen addition in 99.999% argon atmosphere in our glove box. The films are also readily dissolved in deionized water at open circuit potential, though do not noticeably further corrode in dry air. At the start of the electrochemical measurements the system was polarized under reductive polarization of  $-1.2 \text{ V}$  in order to dissolve the formed surface oxide layer. Fig. 2 shows the electrochemical impedance phase angle diagrams for the 100 nm Pb|EMImBF<sub>4</sub> system showing the initial (measured 5 min after polarization begins) and fully reduced (measured after 15 minute cycling of potential between  $-1.6$  and  $-1 \text{ V}$ ) surface states. Of particular note is the extremely low frequency area below 0.1 Hz that shows the faradaic nature in the case of the initial surface state, while mixed kinetics are established for the stable, fully reduced Pb film electrode surface state. This change is also accompanied by a small increase in differential capacitance, which is to be expected for oxide reduction. It is important to point out that the oxide reduction process in dry IL is a time-consuming process and does not proceed instantly as is the case for Pb surface oxide reduction in aqueous electrolytes. The application of dry ionic liquids to lead-acid batteries can also be seen to be limited by the slow kinetics of oxide reduction reaction. This also highlights the necessity to study processes at such low frequencies to ensure the flowing current is due to EDL charging processes and not to residual faradic reactions. The minimal phase angles established for the system ( $<-88^\circ$ ) show nearly ideal capacitive behavior with small deviations probably caused by ultra-trace amounts of O<sub>2</sub>, H<sub>2</sub>O and halide-ions or some oxidized areas remained. A phase angle of  $-90^\circ$  for the Bode

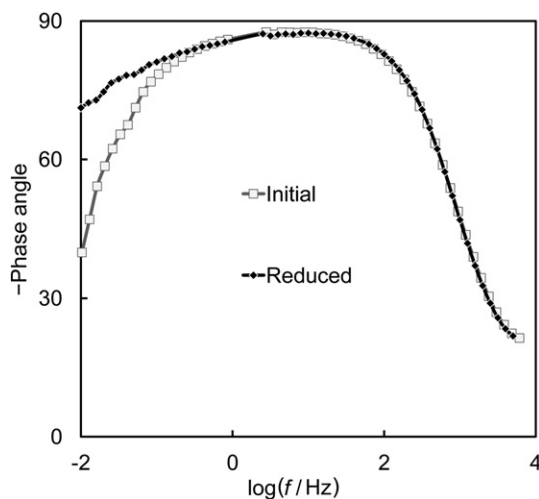


Fig. 2. Electrochemical impedance phase angle diagrams for 100 nm Pb|EMImBF<sub>4</sub> system recorded at  $-1.2 \text{ V}$ . Spectra for initial (oxidized) and fully reduced Pb surface states are shown.

Download English Version:

<https://daneshyari.com/en/article/4908276>

Download Persian Version:

<https://daneshyari.com/article/4908276>

[Daneshyari.com](https://daneshyari.com)