



Combined cyclic voltammetry and in situ electrochemical atomic force microscopy on lead electrode in sulfuric acid solution with or without lignosulfonate

Nobumitsu Hirai^{a,*}, Satoshi Kubo^b, Kengo Magara^b

^a Department of Material and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, 565-0871 Osaka, Japan

^b Department of Chemical Utilization, Forestry and Forest Products Research Institute, 1 Matsunosato, Tsukuba, Ibaraki 305-8687, Japan

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ABSTRACT

The effect of lignosulfonate (LS) on electrochemical reaction of lead electrode (as a model of negative electrode) has been investigated in 1 M, 3 M, or 7.1 M H₂SO₄ aqueous solution with 0, 10, 100 or 1000 mg l⁻¹ of LS using cyclic voltammetry (CV) combined with in situ electrochemical atomic force microscopy (EC-AFM), as well as rotating ring disk electrode (RRDE). The anodic peaks of the CVs, which correspond to overall reaction of $\text{Pb} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 + 2\text{e}^-$, shifted positive when LS was added or the concentration of H₂SO₄ was lower. The anodic capacities of the CVs increased with addition of LS when the concentration of H₂SO₄ was lower. When LS was added, the anodic capacities of the CVs usually increased especially in less concentrated H₂SO₄ solution at higher sweep rate, while the anodic capacity slightly decreased in 7.1 M H₂SO₄ solution with addition of LS at sweep rate of 10 mV min⁻¹; that is, in most concentrated H₂SO₄ solution at lower sweep rate in this paper. Two cathodic peaks of the CVs were observed when LS was added, and the peak at lower potential shifted more negative with increase of LS. Lead sulfate crystals dissolved at more negative potential with increase of LS. LS up-took Pb²⁺ ions in H₂SO₄ aqueous solution during discharging.

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1. Introduction

Expanders, such as lignosulfonate (LS), are indispensable additives for negative electrode of lead acid battery with high performance. Although a lot of investigations [1–46] have been carried out on the effect of the expanders in lead acid battery, a comprehensive understanding of the behavior of the expanders is still lacking. For example, some researchers have demonstrated the lead sulfate crystals become larger in the presence of the expander [18,26,42], while others have reported the opposite effect [13,37]. A detailed knowledge of the mechanism of the expanders' effect is therefore indispensable for developing new expanders. This work was performed to investigate the effect of LS on electrochemical reaction of lead electrode (as a model of negative electrode) in sulfuric acid solution using cyclic voltammetry (CV) combined with in situ electrochemical atomic force microscopy (EC-AFM), as well as rotating ring disk electrode (RRDE).

2. Experimental

2.1. Lignosulfonate

LS used in this paper was sodium salt of lignosulfonic acid (Aldrich, No. 47103-8), although sodium salt of partially desulfonated lignosulfonic acid, such as Vanispeare A, Vanillex N, and so on, is usually used in the actual lead acid batteries. Solubility of LS in H₂SO₄ aqueous solution was estimated using total organic carbon analyzer (Shimadzu Corporation). About 94%, 75% and 94% of LS was dissolved in 1 M (s.g.1.06), 3 M (s.g.1.18) and 7.1 M (s.g.1.40) H₂SO₄ solution.

2.2. Cyclic voltammetry and electrochemical atomic force microscopy

Electrochemical cell used for CV and EC-AFM is almost the same as described in the previous papers [37,42,47]. Working and counter electrodes used for CV and EC-AFM are a lead sheet (purity: 99.999%, apparent surface area: 20 mm², thickness: 0.5 mm) and PbO₂ powders, respectively. Reference electrode used in this paper

* Corresponding author. Tel.: +81 6 68797468; fax: +81 6 68797468.
E-mail address: nhirai@mat.eng.osaka-u.ac.jp (N. Hirai).

is a Hg/Hg₂SO₄ electrode, with respect to which all potentials in this paper are reported. The electrolyte used is 1 M, 3 M, or 7.1 M H₂SO₄ aqueous solution with 0, 10, 100 or 1000 mg l⁻¹ of LS. In order to reduce any oxides on the lead sheet, a potential of -1.2 V was applied for more than 30 min before the experiments. The sweep rate of the CVs is 10 mV min⁻¹, 50 mV min⁻¹, 10 mV s⁻¹ or 50 mV s⁻¹. Three cycles CV operation was applied to the working electrode in this experiment, but the experimental data shown here were obtained during the first cycle. All the experiments shown here were performed at room temperature. The capturing rate was 128 s per each AFM image and the AFM observation area was 10 μm × 10 μm.

2.3. Rotating ring disk electrode (RRDE)

RRDE [48,49] was used for the analysis of Pb²⁺ concentration near the Pb electrode surface in 1 M H₂SO₄ aqueous solution with or without LS during anodic polarization. Inside and outside diameters of ring electrode and diameter of the disc electrode were 5 mm, 7 mm and 4 mm, respectively. During the experiment, potential of ring electrode was always controlled -1.2 V (vs. Hg/Hg₂SO₄), where both H⁺ and dissolved Pb²⁺ in the solution were reduced. First, current of disc electrode was controlled at -30 μA for more than 30 min, which can be considered to be enough time for the reduction of oxide and sulfate initially formed on ring and disc electrode. And then, current of disc electrode was changed from -30 μA to 3 μA in order to start discharging. After starting discharging, the change of ring current, which corresponds to reduction of dissolved Pb²⁺ in the solution, was measured.

3. Results and discussion

3.1. Anodic scans of CV combined with in situ EC-AFM

Fig. 1 show the first anodic scans of CVs in 1 M, 3 M, and 7.1 M H₂SO₄ solution with or without 100 mg l⁻¹ of LS at sweep rate of (a) 10 mV min⁻¹ and (b) 50 mV s⁻¹. It is found from the CVs that the anodic peaks, which correspond to overall reaction of Pb + SO₄²⁻ → PbSO₄ + 2e⁻, shift positive when LS is added or the concentration of H₂SO₄ is lower. It is also found from the CVs that anodic capacity increase with addition of LS when the concentration of H₂SO₄ is lower. Fig. 2 describe the anodic capacities calculated from the anodic scans of the CVs in (a) 1 M, (b) 3 M, and (c) 7.1 M H₂SO₄ solution as a function of concentration of LS. As

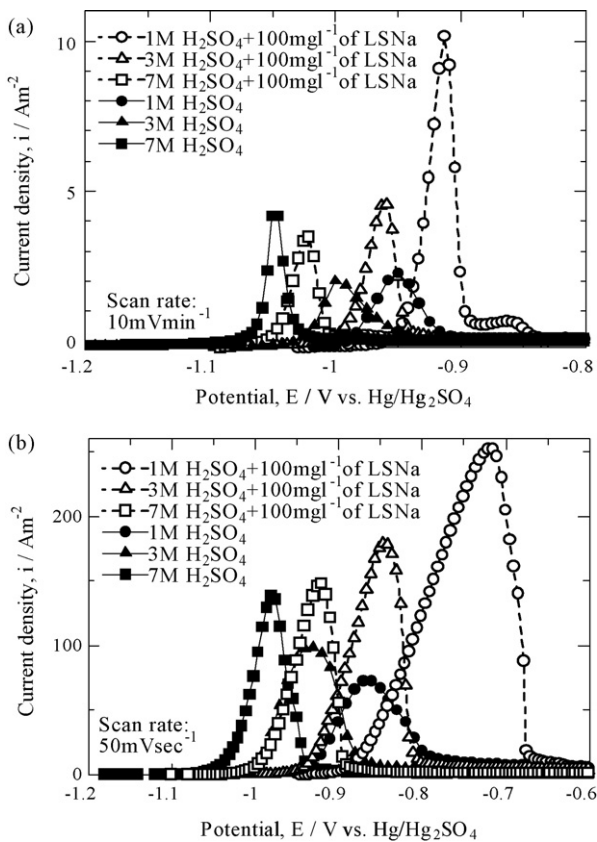


Fig. 1. First anodic scans of CVs in 1 M, 3 M, and 7.1 M H₂SO₄ solution with or without 100 mg l⁻¹ of LS at sweep rate of (a) 10 mV min⁻¹ and (b) 50 mV s⁻¹.

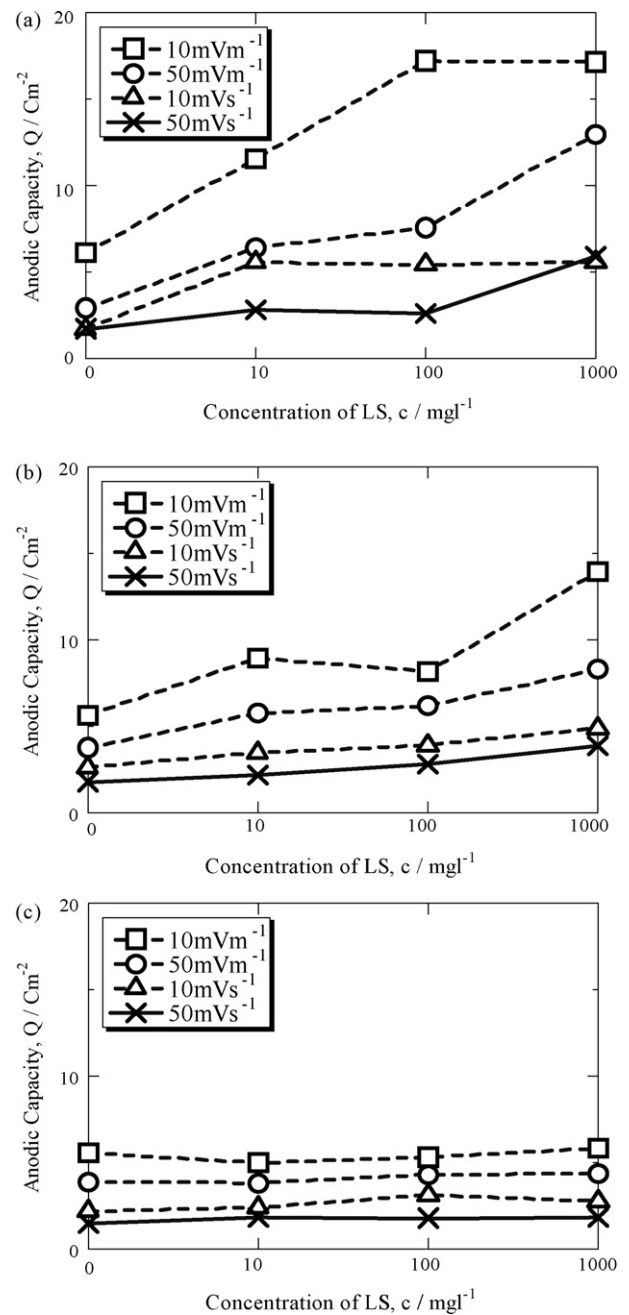


Fig. 2. Anodic capacities calculated from the anodic scans of the CVs in (a) 1 M, (b) 3 M, and (c) 7.1 M H₂SO₄ solution as a function of concentration of LS.

shown in Fig. 2(a), anodic capacity in 1 M H₂SO₄ solution increases with the concentration of LS, while anodic capacity in 7.1 M H₂SO₄ solution is almost constant at any concentration of LS as indicated in Fig. 2(c). When LS was added, the anodic capacity increased especially in less concentrated H₂SO₄ solution at higher sweep rate. It is noteworthy that the anodic capacity slightly decreases in 7.1 M H₂SO₄ solution with addition of LS at sweep rate of 10 mV min⁻¹.

Fig. 3 indicates the first anodic scans of CVs, and Figs. 4 and 5 shows continuous in situ EC-AFM images in 1 M H₂SO₄ solution with and without 1000 mg l⁻¹ of LS, respectively. The sweep rate of the CVs was 10 mV min⁻¹. The marked (a)–(h) on the CVs in Fig. 3 correspond to the potential region of AFM images (a)–(h) in Figs. 4 and 5. There is an anodic peak at about -0.9 V in the solution with 1000 mg l⁻¹ of LS in Fig. 3. As shown in Figs. 4(e) and (f), many large lead sulfate crystals deposited at the top of the anodic peak. This means that this anodic reaction can explain by solution-

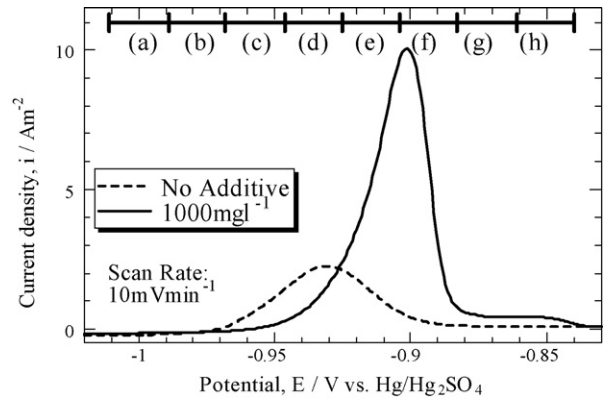


Fig. 3. First anodic scans of CVs in 1 M H₂SO₄ solution with and without 1000 mg l⁻¹ of LS. The sweep rate of the CVs was 10 mV min⁻¹.

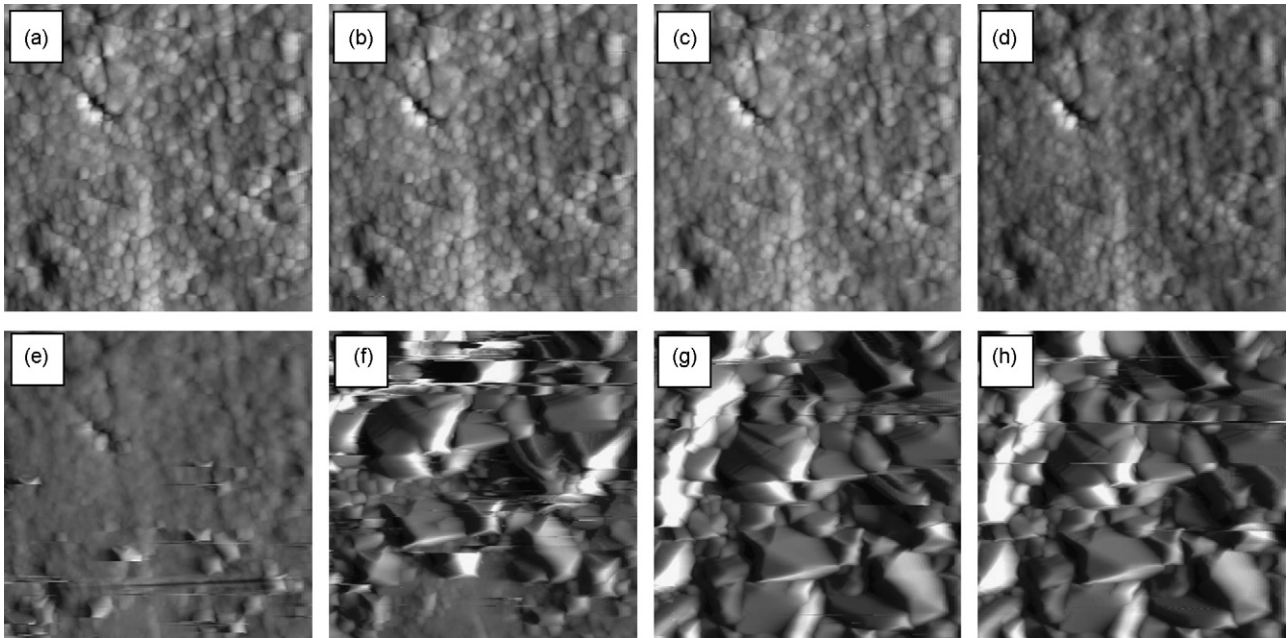


Fig. 4. Continuous in situ EC-AFM images during first anodic scans of CVs in Fig. 3 in 1 M H₂SO₄ solution with 1000 mg l⁻¹ of LS.

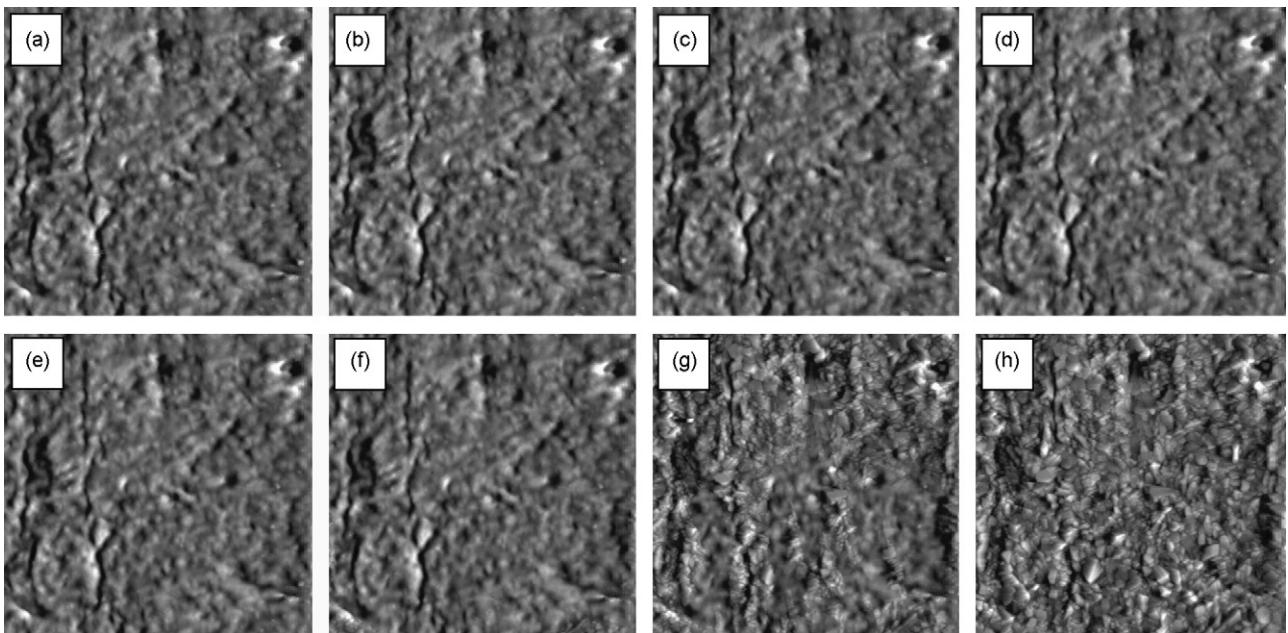


Fig. 5. Continuous in situ EC-AFM images during first anodic scans of CVs in Fig. 3 in 1 M H₂SO₄ solution without LS.

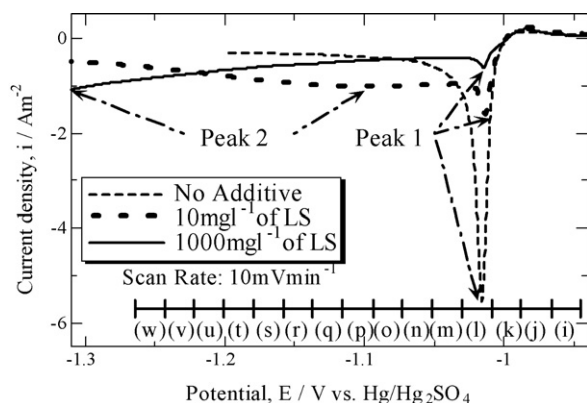


Fig. 6. Cathodic scans of the first cycle of CVs between -1.3 V and -0.8 V in 1 M H_2SO_4 solution with 0 , 10 , 1000 mg l^{-1} of LS at sweep rate of 10 mV min^{-1} . The marked (i)–(w) on the CVs in Fig. 6 corresponds to the potential region of AFM images (i)–(w) in Figs. 7–9.

precipitation mechanism, which was proposed by Archdale et al. [9,48,50] and Weininger [51], and was confirmed by in situ EC-AFM observation in 1.6 M H_2SO_4 solution without additive [47], and in 5 M H_2SO_4 solution with or without 20 ppm of Vanillex N [42].

On the other hand, there is an anodic peak at about -0.93 V in the solution without LS in Fig. 3, but morphological change of lead surface is mainly observed at about -0.87 V as shown in Fig. 5. This difference of the potentials at the anodic peak and at which the morphological change is observed means that this anodic reaction in 1 M H_2SO_4 solution without LS at sweep rate of 10 mV min^{-1} cannot explain by solution-precipitation mechanism. This reaction might explain by solid-state reaction [9,10,48,50]. This assumption is consistent with the previous works [9,10].

3.2. Cathodic scans of CV with combined in situ EC-AFM

Fig. 6 indicates cathodic scans of the first cycle of CVs between -1.3 V and -0.8 V, and Figs. 7–9 shows continuous in situ EC-AFM

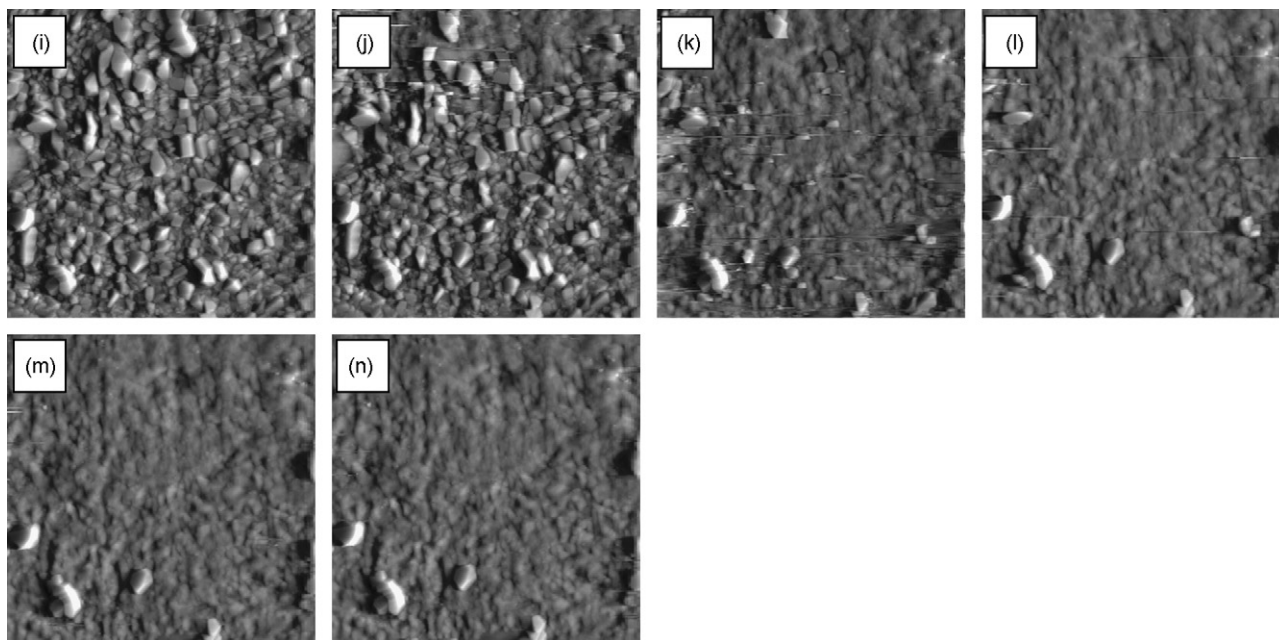


Fig. 7. Continuous in situ EC-AFM images during cathodic scans of the first cycle of CVs in 1 M H_2SO_4 solution without LS at sweep rate of 10 mV min^{-1} . The marked (i)–(n) on the CVs in Fig. 6 corresponds to the potential region of AFM images (i)–(n) in Fig. 7.

images in 1 M H_2SO_4 solution with 0 , 10 , 1000 mg l^{-1} of LS at sweep rate of 10 mV min^{-1} , respectively. The marked (i)–(w) on the CVs in Fig. 6 corresponds to the potential region of AFM images (i)–(w) in Figs. 7–9. Cathodic peaks observed in Fig. 6 correspond to overall reaction of $\text{PbSO}_4 + 2e^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$ and/or Pb^{2+} (in the solution) $+ 2e^- \rightarrow \text{Pb}$. As shown in Fig. 6, two cathodic peaks (peaks 1 and 2 in Fig. 6) are observed when LS is added, and the peak at lower potential (peak 2 in Fig. 6) shift more negative with increase of LS. As shown in Figs. 7–9, almost all lead sulfate crystals dissolve at about -1.05 V, -1.07 V and -1.27 V, respectively. These results suggest that the peak 1 corresponds to the rapid reduction of Pb^{2+} in the solution (Pb^{2+} (in the solution) $+ 2e^- \rightarrow \text{Pb}$) and the peak 2 corresponds to the slow dissolution of lead sulfate crystals ($\text{PbSO}_4 \rightarrow \text{Pb}^{2+} + \text{SO}_4^{2-}$), followed by the rapid reduction of Pb^{2+} (Pb^{2+} (from PbSO_4) $+ 2e^- \rightarrow \text{Pb}$) when LS was added. When LS is not added, peak 2 is not observed as shown in Fig. 6. That was maybe because the peak 1 of the CV in the solution without LS was a combination of the peaks 1 and 2 of the CVs in the solution with LS.

3.3. Rotating ring disk electrode (RRDE)

It is widely authorized that LS up-takes Pb^{2+} ions [5] by sulfonic acid groups [46] as complexes containing LS and Pb [40,43], however, it is still unobvious that LS up-takes Pb^{2+} ions in H_2SO_4 aqueous solution under potential control. In this paper, RRDE was used for the analysis of Pb^{2+} concentration near the Pb electrode surface in 1 M H_2SO_4 aqueous solution during anodic polarization. Fig. 10 shows ring current change of RRDE in 1 M H_2SO_4 solution with and without 100 mg l^{-1} of LS as a function of time. Open marks (open circle, open diamond, open triangle, open square) correspond to 4 runs of the results without LS, while filled marks (filled circle, filled diamond, filled triangle, filled square) correspond to 4 runs of the results with 100 mg l^{-1} of LS. Current of disc electrode was changed from -30 μA to 3 μA at 10 s and ring current change is referred to the ring current at 10 s in Fig. 10. As shown in Fig. 10, ring current in the solution with 100 mg l^{-1} of LS increased slower than that in the solution without LS although disc current was 3 μA

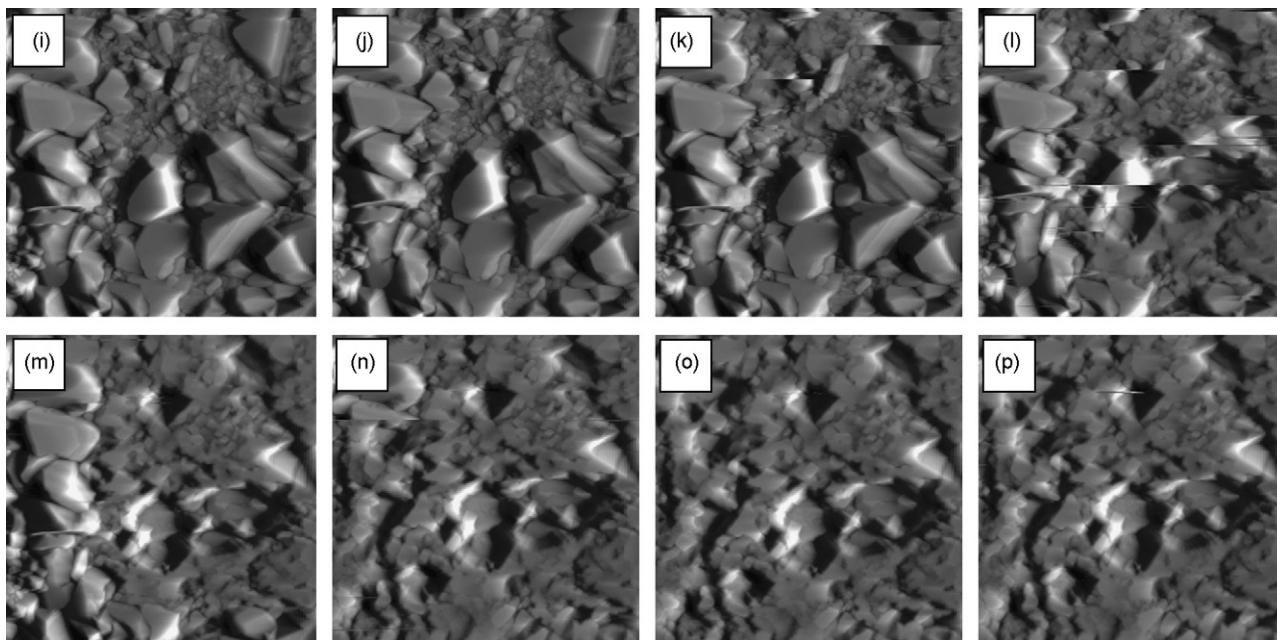


Fig. 8. Continuous in situ EC-AFM images during cathodic scans of the first cycle of CVs in Fig. 6 in 1 M H₂SO₄ solution with 10 mg l⁻¹ of LS at sweep rate of 10 mV min⁻¹. The marked (i)–(p) on the CVs in Fig. 6 corresponds to the potential region of AFM images (i)–(p) in Fig. 8.

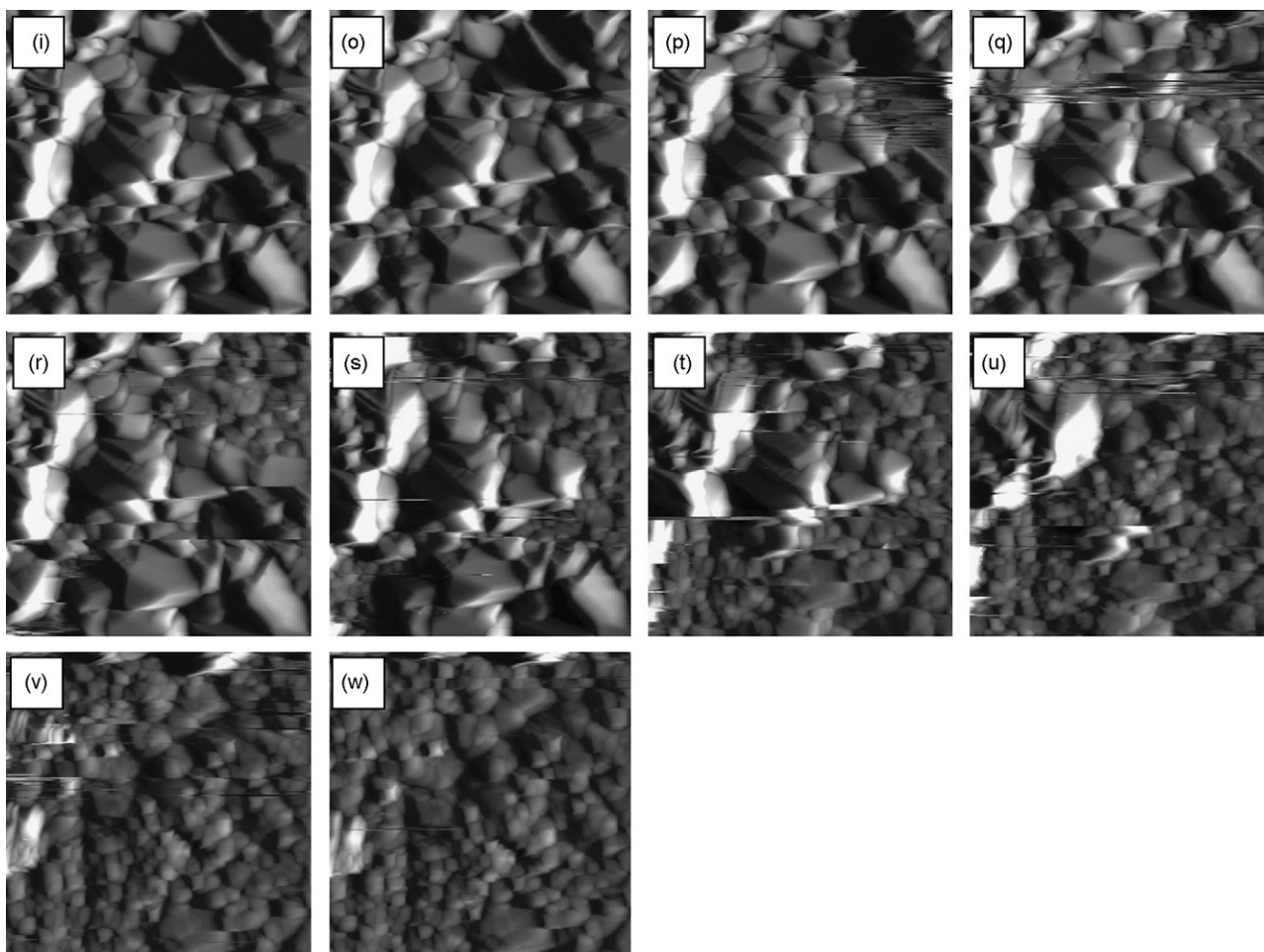


Fig. 9. Continuous in situ EC-AFM images during cathodic scans of the first cycle of CVs in Fig. 6 in 1 M H₂SO₄ solution with 1000 mg l⁻¹ of LS at sweep rate of 10 mV min⁻¹. The marked (i), (o)–(w) on the CVs in Fig. 6 corresponds to the potential region of AFM images (i), (o)–(w) in Fig. 9.

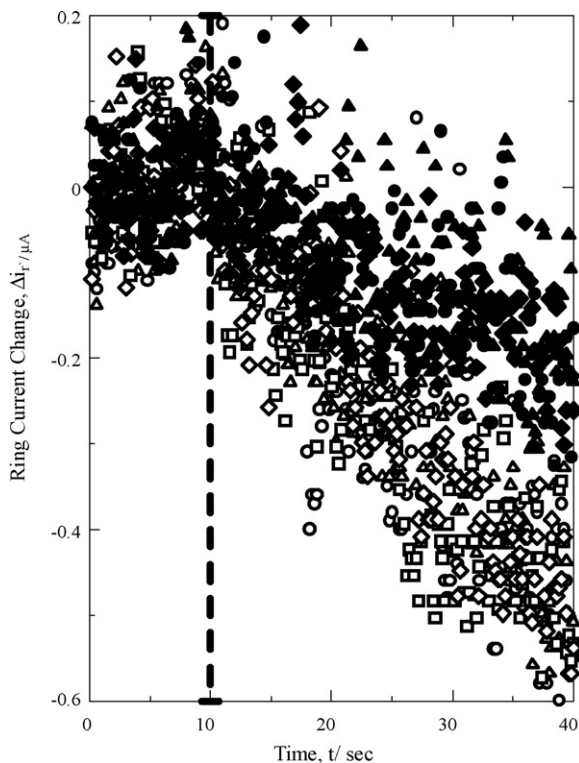


Fig. 10. Ring current change of RRDE in 1 M H₂SO₄ solution with and without 100 mg l⁻¹ of LS as a function of time. Open marks (open circle, open diamond, open triangle, open square) correspond to 4 runs of the results without LS, while filled marks (filled circle, filled diamond, filled triangle, filled square) correspond to 4 runs of the results with 100 mg l⁻¹ of LS.

in both cases. These results are explained in terms of the uptakes of Pb²⁺ ions by LS.

4. Summary

The effect of LS on electrochemical reaction of lead electrode (as a model of negative electrode) has been investigated in 1 M, 3 M, or 7.1 M H₂SO₄ aqueous solution with 0, 10, 100 or 1000 mg l⁻¹ of LS using CV combined with in situ EC-AFM, as well as rotating ring disk electrode (RRDE). The main results obtained are shown below.

- (1) The anodic peaks of the CVs, which correspond to overall reaction of $\text{Pb} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 + 2\text{e}^-$, shifted positive when LS was added or the concentration of H₂SO₄ was lower.
- (2) The anodic capacities of the CVs increased with addition of LS when the concentration of H₂SO₄ was lower.
- (3) When LS was added, the anodic capacities of the CVs usually increased especially in less concentrated H₂SO₄ solution at higher sweep rate, while the anodic capacity slightly decreased in 7.1 M H₂SO₄ solution with addition of LS at sweep rate of 10 mV min⁻¹; that is, in most concentrated H₂SO₄ solution at lower sweep rate in this paper.
- (4) Two cathodic peaks of the CVs were observed when LS was added, and the peak at lower potential shifted more negative with increase of LS.
- (5) Lead sulfate crystals dissolved at more negative potential with increase of LS.

- (6) LS up-took Pb²⁺ ions in H₂SO₄ aqueous solution during discharging.

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