



Electro-deposition behavior and proof-of-concept operation in methanesulfonic acid-based crude lead electro-refining

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Received 19 April 2022; accepted 15 August 2022

Abstract: A promising methanesulfonic acid (MSA) system, in lieu of conventional fluosilicic acid system, for green and efficient electro-refining of Pb, was proposed, due to its low volatility, low corrosivity, desired thermal stability and high conductivity. The electro-deposition behavior of the MSA-based Pb electro-refining (MPR) was explored, including its operation mechanism, reaction reversibility, nucleation, and growth mode. Based on cyclic voltammetry (CV) and chronoamperometry (CA), the diffusion-controlled and irreversible lead deposition process of MPR was revealed, and the theoretical model of MPR lead deposition nucleation and growth with transient nucleation was established. The bench-scale proof-of-concept operation of MPR achieved energy consumption of 104.22 kW·h/t Pb and current efficiency of 99.24%, which was competitive with the energy consumption of 120 kW·h/t Pb and current efficiency of 95% for H₂SiF₆ system. The bench-scale operation of MPR obtained a smooth and compact deposit sample with Pb purity of 99.9925%, which satisfied the standard of Pb ingot (GB/T 469—2013) of 99.97%.

Key words: lead electro-refining; methanesulfonic acid; electro-deposition behaviour; electrochemical analysis; cathodic morphology

1 Introduction

Lead (Pb) and its compounds are widely used in electrical industry, medical and health, and construction fields, etc [1,2]. The Pb sulfide concentrate undergoes the bath smelting, including oxidizing and desulphurizing processes, to obtain the primary crude Pb and the high Pb slag which reduced to produce secondary crude Pb [3,4]. Subsequently, the obtained crude Pb successively undergoes the pyro-refining to de-copper, and the electro-refining to produce qualified Pb deposits. At present, the electro-refining of crude Pb mainly employs the Betz method [5,6], using fluosilicic acid

(H₂SiF₆)-Pb fluorosilicate solution as the electrolyte. However, the further development of this method is severely hindered by the disadvantages of high volatility of H₂SiF₆, undesired thermal stability and terrible operating environment. With increasing green initiative, developing a green electro-refining system for crude Pb production is imperative.

Some potentially-viable systems, such as chloride, acetate, nitrate, fluoroboric acid and alkaline solution, for Pb electro-refining have been explored to advance it. For instance, the Federal Bureau of Mines employed various chloride systems for Pb electro-refining [7]. NIKOLIC et al [8] and KHALIL and JALIL [9] adopted an acetate system to obtain high purity lead under the conditions

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DOI: 10.1016/S1003-6326(23)66205-3

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of 2 g/L gelatin additive, 2.5 mol/L acetic acid and electrolysis temperature of 40–50 °C. AVELLANEDA et al [10] investigated the effect of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ on the opto-electrochromic properties of electrodeposited Pb films. GUI [11] proposed a fluoroboric-acid system for electro-plating Pb at high current efficiency plus smooth, uniform and dense coatings. WONG and ABRANTES [12] investigated the electro-deposition behavior of Pb in alkaline medium and revealed the evolution of nucleation mode from the continuous nucleation to the instantaneous nucleation as a function of Pb concentration. Despite extensive studies on the above-mentioned systems for Pb electro-refining, they were still at the research stage with various technical and economic challenges requiring overcoming.

In this work, we proposed a promising methanesulfonic acid (MSA) system for green and efficient electro-refining of Pb. The merits of “green” and high-efficiency originate from its properties of low volatility, low corrosivity, thermal stability and high conductivity [13,14]. This facilitates the application of MSA in electro-plating, such as electro-plating of tin [15], and electro-plating of nano-Pb oxide for oxidation of organic pollutants [16]. Especially, the MSA system was used to electro-deposit Pb [17–19], which achieved efficient deposition with flat and compact deposits.

In this work, we explored the electro-deposition behavior and the technical feasibility of MSA-based Pb electro-refining (MPR), with the aim to advance it towards practical application. The electro-deposition behavior of MPR was investigated, including its operation mechanism, reaction reversibility, nucleation and growth mode. The bench-scale proof-of-concept operation was performed. The result indicates that the MPR process was superior to the H_2SiF_6 -based electro-refining of crude Pb.

2 Experimental

2.1 Materials

The main raw materials for the test were MSA (BASF New Material Co., Ltd.), lead oxide (Tianjin Kermel Chemical Reagent Co., Ltd.), phosphate (H_3PO_4), sodium lignosulfonate (Aladdin Chemical Reagents Co., Ltd.) and gelatin. The reagents used

were analytical pure. The anode was crude Pb, which was produced by molten lead produced by pyro-refining process of lead smelter, and the cathode was titanium plate. Chemical composition of crude Pb anode is shown in Table 1.

Table 1 Chemical composition of crude lead anode (wt.%)

Pb	Sn	Zn	As	Sb
97.7897	0.55	0.011	0.0034	0.81
Bi	Fe	Ag	Cu	
0.65	0.0009	0.075	0.11	

2.2 Electrochemical measurement

The electrochemical test equipment was the electrochemical workstation of CHI760E. The “L”-type glassy carbon electrode with exposure area of 0.07 cm², the platinum plate (1 cm²) and the saturated calomel electrode were used as the working electrode, the counter electrode and the reference electrode, respectively. To circumvent the mutual contamination between reference electrode and electrolyte, a salt bridge filled with saturated potassium chloride solution was used. Before each test, the glassy carbon electrode was polished by metallographic sandpaper of 1000, 1500 and 3000 grit in sequence and then subjected to ultrasonic treatment for 15 min, while the platinum-plate electrode was immersed in nitric acid for about 10 min to ensure its surface adequately clean. When a stable open-circuit potential was obtained (<1.0 mV variation over 1 min), the test began. Firstly, the linear sweep voltammetry was measured at a scanning rate of 20 mV/s. Then, the cyclic voltammogram curve was swept at the scanning rate of 20–150 mV/s. Finally, in the current–time transient, the applied potential was set between –0.46 and –0.58 V, the concentration of Pb^{2+} was 0–150 g/L, the concentration of MSA was 0–190 g/L, the concentration of H_3PO_4 was 0–6 mL/L, and the temperature was 25–45 °C.

2.3 Bench-scale operation of MPR

The sample solution was composed of MSA, Pb oxide and additives. The crude Pb and titanium plate were utilized as the anode (12 cm × 7.2 cm × 1.7 cm) and the cathode (18.5 cm × 9.5 cm × 0.3 cm), respectively. The electrolysis was carried out in self-made PVC electrolytic cell (17 cm ×

16.2 cm × 13 cm). The reaction temperature was controlled by a thermostatic water bath, and the circulation rate of electrolyte was controlled by peristaltic pump. The conditions of MSA system were as follows: 100 g/L Pb²⁺, 60 g/L MSA, current density of 180 A/m², polar distance of 4 cm, flow rate of 2.92 mL/(min·A), operation temperature of 45 °C, electrolytic time of 8 h, and GE of 2 g/L or SL of 1 g/L. The conditions of H₂SiF₆ system were as follows: 55–120 g/L Pb²⁺, 80–120 g/L MSA, polar distance of 9 cm, current density of 170–190 A/m², flow rate of 22–35 L/min, GE of 400–1000 g/t Pb, and SL of 400–1000 g/t Pb.

Before each electrolysis, the cathode and anode plates were polished sequentially with sandpapers of 600, 800, 1000 and 2000 grit, and then soaked and washed with anhydrous ethanol and deionized water. Once the electrolysis started, the voltage value was recorded every 15 min. At the end of electrolysis, the Pb deposit sample was subjected to photographing and SEM observation (MIRA4 LMH scanning electron microscope produced by TESCAN Company of Czech Republic). The Pb deposit sample was dissolved into nitric acid solution, which was characterized by ICP-AES (ICPE-9800 inductively coupled plasma atomic emission spectrometer produced by Shimadzu of Japan).

The current efficiency of the bench-scale operation was calculated by

$$\eta = \frac{m}{nqIt} \times 100\% \quad (1)$$

where η is the current efficiency, %; n is the number of electrons involved in the electrode reaction; m is the mass of Pb deposit, g; I is the current, A; t is the electrolysis time, h; q is the electrochemical equivalent of Pb, 3.867 g/(A·h).

The energy consumption was calculated by

$$W = \frac{1000U}{\eta q} \times 100\% \quad (2)$$

where W is the electric energy consumption, kW·h/t, and U is the average cell voltage, V.

3 Results and discussion

3.1 Electro-deposition behavior of MPR

3.1.1 Electro-deposition principle of MPR

We performed cyclic voltammogram (CV) to

preliminarily gain insights into the electro-deposition principle of MPR. Figure 1 shows no obvious hydrogen evolution current, at potentials more positive than −0.8 V. This indicates that the Pb deposition is prior to the hydrogen evolution thermodynamically. Additions of Pb²⁺ ions contribute to the suddenly steep increase in cathodic current density from −0.46 V due to the rapid deposition of Pb. The cathodic peak at −0.64 V is due to the concentration polarization on electrode surface. Note that Pb deposit is clearly observed on surface within the cathodic-current-rise range and the curve without Pb ions lacks the current-rise range. This confirms that the current density soar is attributed to the Pb deposition. After reversing from −0.75 V into a positive direction, the anodic current density appears and gradually increases at −0.43 V, corresponding to a Pb dissolution process. When the anodic current density reaches an anode (oxidation) peak at −0.18 V, the Pb dissolution attains the fastest rate. As a result, after reversing at 0.4 V, the scan gradually returns back to the starting potential (0.4 V), thus closing the cycle. It is worth mentioning that two points of intersection denoted as O appear, the phenomenon of which is called nucleation ring. This indicates that the initial deposition of Pb²⁺ undergoes a process of nucleation and growth [20–23]. Moreover, the peak potential difference (601 mV) is much greater than the theoretical value of $2.303RT/(nF)$ (23.30 mV at $n=2$ and $T=30$ °C). This reflects the irreversibility of our system, and the double electron transfer process of Pb²⁺/Pb(s) is completed in one step.

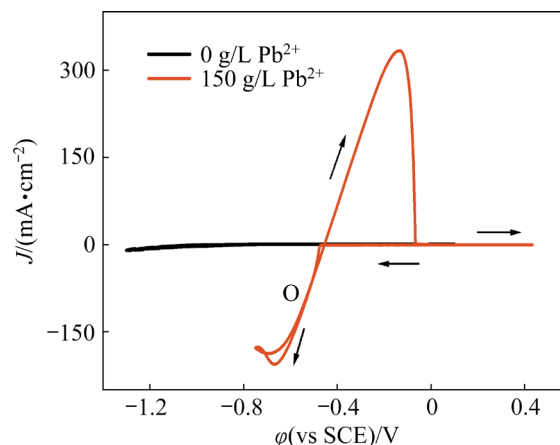


Fig. 1 Cyclic voltammograms in 50 g/L MSA solution containing 0 g/L or 150 g/L Pb²⁺ and 1 mL/L H₃PO₄ at 30 °C under scanning rate of 20 mV/s

To further understand the irreversibility of Pb^{2+} deposition, the CV curves at different scanning rates were measured (Fig. 2). Increasing scanning rate increases the cathodic peak current density, which is consistent with the characteristics of irreversible reaction. For irreversible system, the electrode reaction was controlled by diffusion step when the dependence of cathodic peak current density (J_p) and the peak potential (ϕ_p) on the potential scanning rate (ν) conforms to the following equations [24]:

$$J_p = 0.4958(nF)^{2/3}(\alpha D\nu)^{1/2}(RT)^{-1/2}AC^* \quad (3)$$

$$\phi_p = \phi^0 - \frac{RT}{\alpha nF} \left[0.780 + \ln\left(\frac{D^{1/2}}{k_0}\right) + \ln\left(\frac{\alpha F\nu}{RT}\right)^{1/2} \right] \quad (4)$$

where F is the Faraday constant (96485 C/mol); α is the transfer coefficient; D is the diffusion coefficient (cm^2/s); ϕ^0 is the standard electrode potential (V); R is the gas constant (8.314 J/(mol·K)); T is the thermodynamic temperature (K); A is the area of the working electrode (cm^2); C^* is the bulk concentration of Pb^{2+} ions (mol/L); k_0 is the standard rate constant of the different phase (cm/s). The ϕ_p and J_p obtained at different scanning rates are listed in Table 2. The relationships of the ϕ_p with $\lg \nu$ and the J_p with $\nu^{1/2}$ were determined with excellent correlations ($R^2 > 0.99$) (Fig. 3). Evidently, this well conforms to Eqs. (3) and (4), indicating the irreversibility of the electrode reaction in the MSA system with the diffusion step as the controlled one.

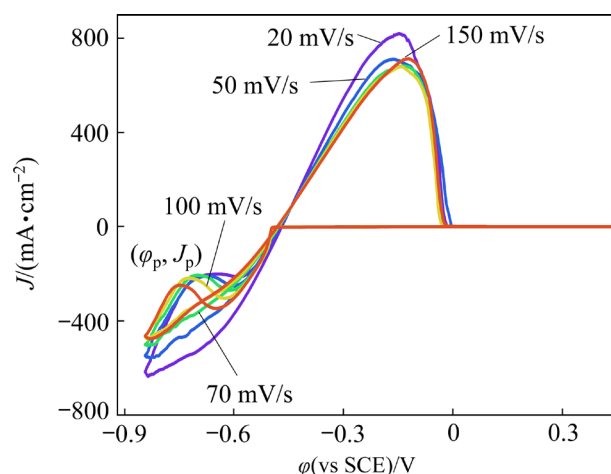


Fig. 2 Cyclic voltammograms in solution containing 50 g/L MSA, 150 g/L Pb^{2+} and 1 mL/L H_3PO_4 at 30 °C under different scanning rates

Table 2 Cathodic peak potential (ϕ_p) and peak current density (J_p) under different scanning rates (ν)

$\nu/(\text{mV} \cdot \text{s}^{-1})$	$\phi_p(\text{vs SCE})/\text{V}$	$J_p/(\text{A} \cdot \text{cm}^{-2})$
20	−0.641	0.232
50	−0.672	0.271
70	−0.693	0.298
100	−0.713	0.332
150	−0.735	0.375

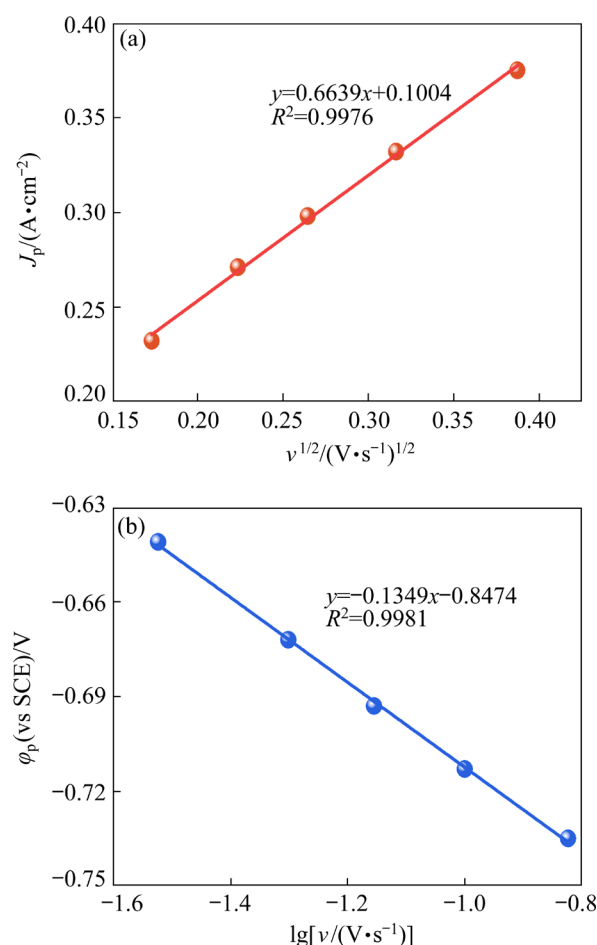


Fig. 3 Relationship of peak current density (a) and peak potential (b) with scanning rate

3.1.2 Nucleation and growth mode of electro-deposition process of MPR

To clarify the nucleation and growth mode of Pb deposition of MPR, the chronoamperometry was adopted to test the current transient curves at different constant potentials. Figure 4(a) shows similar trends for the curves from −0.52 to −0.58 V (vs SCE), in which the current density initially increases to maximum values due to formation and growth of the crystal nuclei, and subsequently decreases due to overlaps of the

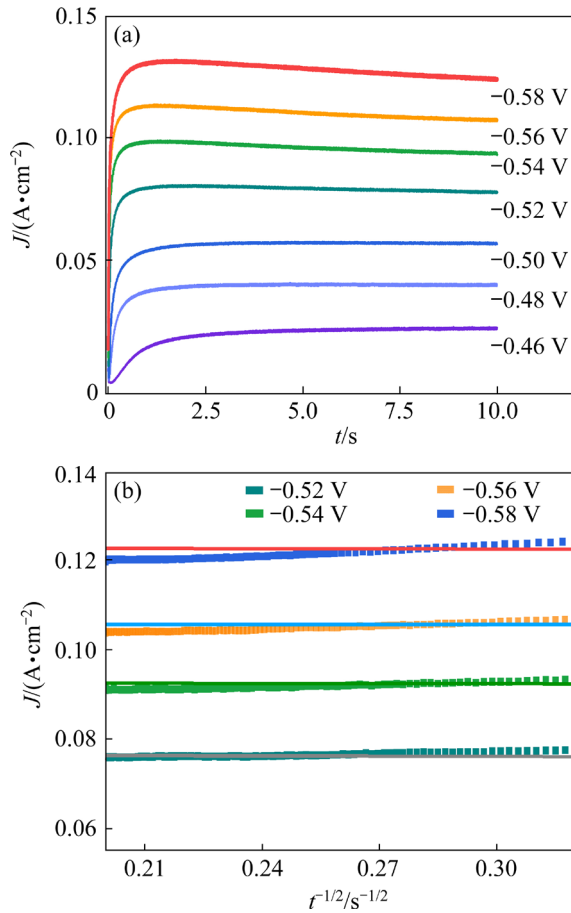


Fig. 4 $J-t$ (a) and $J-t^{-1/2}$ (b) curves at different step potentials in solution containing 50 mol/L MSA, 150 g/L Pb^{2+} and 1 mL/L H_3PO_4 at 30 °C

growth centers, namely, disappearance of the growth centers and regenerations of the new growth centers [25,26]. This phenomenon agrees well with the characteristic of the three-dimensional nucleation mode [25]. In addition, with shifting applied potential towards negative values, the current density increases due to the driven force of overpotential according to the Butler–Volmer equations [27]. It can be found from Figs. 4(a, b) that the current densities at potentials of -0.52 to -0.58 V (vs SCE) showed a good linear relationship with $t^{-1/2}$, which was consistent with the diffusion-controlled model, based on the Cottrell equation [28]:

$$J = nFC(D/\pi)^{1/2} t^{-1/2} \quad (5)$$

where nF is the molar charge transferred in the electro-deposition process, and C is the volume concentration of the electroactive substance. This result also demonstrates the transfer of Pb^{2+} ions in the diffusion layer as rate-determining step at these

potentials.

To explore the three-dimensional nucleation model of the Pb deposition, we introduced the SH model proposed by Benjamin Scharifker and Graham Hills–instantaneous nucleation [29] and continuous nucleation [30], of which dimensionless formula could be described as follows [25]:

(1) Instantaneous nucleation

$$\left(\frac{J}{J_m}\right)^2 = \frac{1.9542}{t/t_m} \{1 - \exp[-1.2564(t/t_m)]\}^2 \quad (6)$$

(2) Continuous nucleation

$$\left(\frac{J}{J_m}\right)^2 = \frac{1.2254}{t/t_m} \{1 - \exp[-2.3367(t/t_m)^2]\}^2 \quad (7)$$

where J_m and t_m are the maximal current density on the curves and the corresponding time, respectively. According to Eqs. (6) and (7), Fig. 5 shows the $(J/J_m)^2 - (t/t_m)$ curves with the instantaneous nucleation and continuous nucleation models. Evidently, the nucleation and growth mode of the deposition process of MPR is closer to the characteristic of instantaneous nucleation.

Figure 6 shows the nucleation rate at different applied potentials, based on the following equation:

$$J_m = nFK' \quad (8)$$

where K' is the nucleation rate. The applied potential has a significant effect on the crystal growth rate, which increases from 4.17 to 6.8 mol/(cm²·s) with decreasing applied potential from -0.52 to -0.58 V. This indicates that the high overpotential as driver force facilitates the crystal growth. Moreover, we calculated the diffusion coefficient, D , based on the Eq. (9) and recorded them in Table 3.

$$J_m^2 t_m = 0.1629(nFC)^2 D \quad (9)$$

With increasing potential from -0.58 to -0.52 V (vs SCE), the D (4.2×10^{-6} – 5.2×10^{-6} cm²/s) varies very little, and the average D is calculated as 4.83×10^{-6} cm²/s.

Pb^{2+} ion concentration, MSA concentration, temperature and phosphoric acid (H_3PO_4) additive are important factors influencing electrochemical behavior. Herein, we investigated the effects of them on the nucleation and growth mode of the deposition process of MPR. Figure 7(a) shows that increasing Pb^{2+} ion concentration from 50 to 150 g/L decreases J_m and increases t_m , indicating

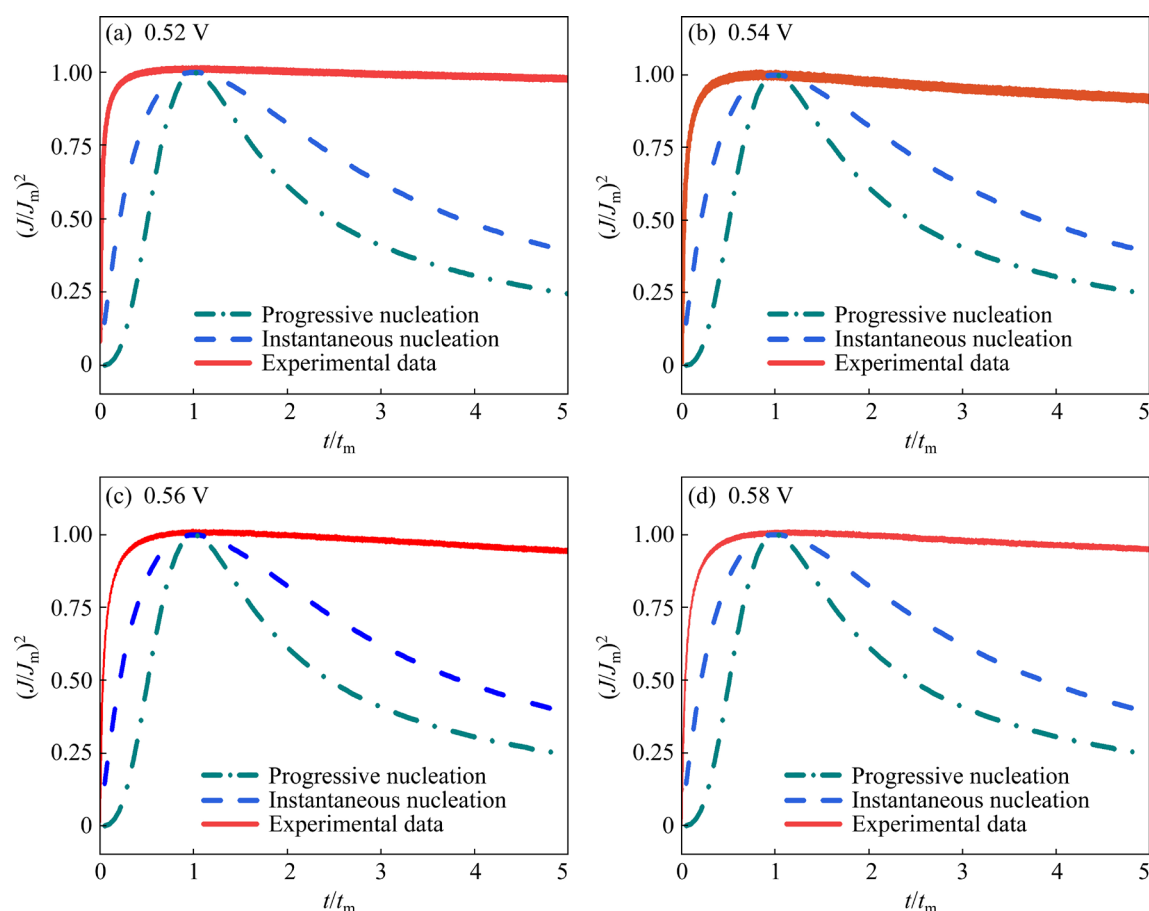


Fig. 5 $(J/J_m)^2-t/t_m$ plots at different step potentials (t_m and J_m were obtained from Fig. 4(a))

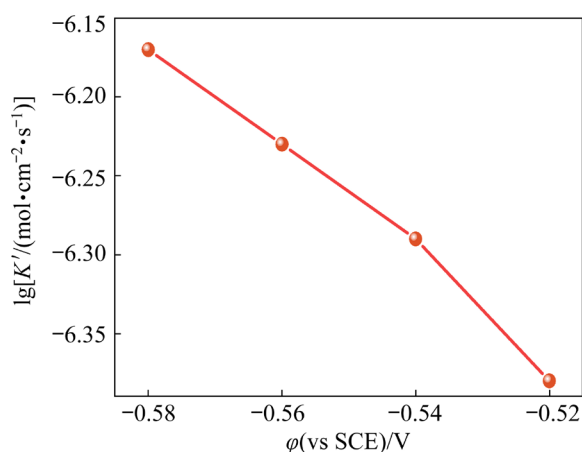


Fig. 6 Nucleation rate (K') in logarithmic scale as function of applied potential

that higher Pb^{2+} ion concentration disfavors the early-stage formation and growth of crystal nuclei. Moreover, with increasing Pb^{2+} ion concentration, steady-state current density (J_{ss}) after the J_m becomes higher. This suggests that higher Pb^{2+} ion concentration facilitates the late-stage growth of deposit that involves overlaps of growth centers. Non-dimensional $(J/J_m)^2-t/t_m$ curves (Figs. 7(b–f))

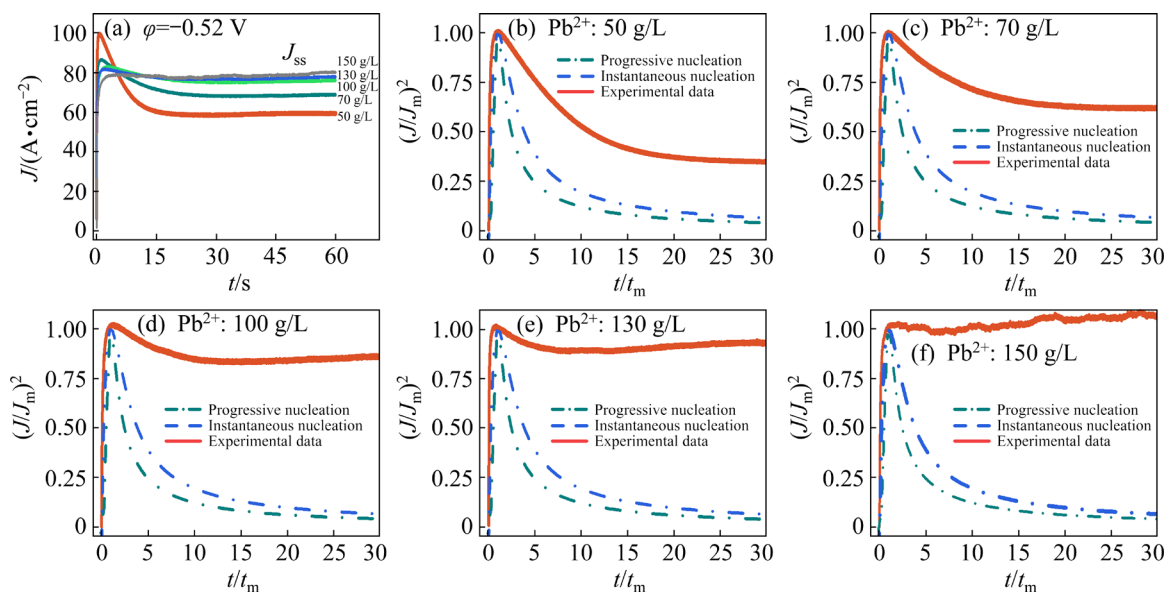
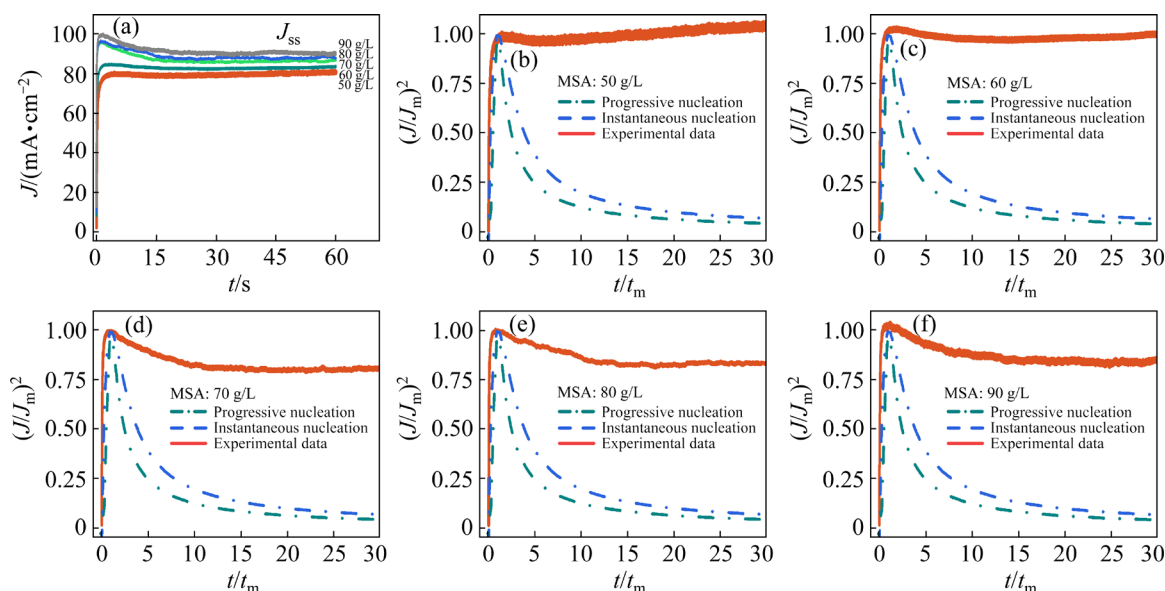
are closer to the theoretical model of instantaneous nucleation, indicating that on the whole, the nucleation and growth mode of Pb deposition in the test system is unchanged with Pb^{2+} ion concentration. Furthermore, at lower Pb^{2+} ion concentration, the experimental non-dimensional curve indicates that the nucleation mode of Pb more conforms to the theoretical mode of instantaneous nucleation.

Figure 8(a) shows that increasing MSA concentration from 50 to 90 g/L increases J_m and J_{ss} , and decreases t_m , suggesting that higher MSA concentration facilitates the overall nucleation and growth process of Pb deposition in the test system. Likewise, the non-dimensional $(J/J_m)^2-t/t_m$ curves (Figs. 8(b–f)) are closer to the theoretical model of instantaneous nucleation, indicating that the nucleation and growth mode of the Pb deposition is basically unchanged with MSA concentration.

Figure 9(a) shows that with increasing solution temperature from 25 to 45 °C, J_m and J_{ss} increase, and t_m decreases, implying that higher temperature favors the overall nucleation and growth process of the Pb deposition. The enhancement effect of

Table 3 Kinetic parameters of Pb electro-crystallization in solution containing 50 mol/L MSA, 150 g/L Pb²⁺ and 1 mL/L H₃PO₄ at 30 °C

φ (vs SCE)/ V	J_m / (mA·cm ⁻²)	t_m /s	$J_m^2 t_m$ / (10 ⁴ mA ² ·s·cm ⁻⁴)	K' / (10 ⁷ mol·cm ⁻² ·s ⁻¹)	lg [K' / (mol·cm ⁻² ·s ⁻¹)]	D / (10 ⁻⁶ cm ² ·s ⁻¹)
-0.52	80.57	2.04	1.3	4.2×10 ⁻⁷	-6.39	4.2
-0.54	98.50	1.59	1.5	5.1×10 ⁻⁷	-6.29	4.8
-0.56	112.64	1.29	1.6	5.8×10 ⁻⁷	-6.23	5.1
-0.58	131.24	0.96	1.7	6.8×10 ⁻⁷	-6.17	5.2

**Fig. 7** J - t transient (a) and $(J/J_m)^2$ - t/t_m (b-f) plots for Pb electro-deposition in solution containing 50 mol/L MSA and 1 mL/L H₃PO₄ at 30 °C with different concentrations of Pb²⁺**Fig. 8** J - t (a) and $(J/J_m)^2$ - t/t_m (b-f) plots for Pb electro-deposition in solution containing 150 g/L Pb²⁺ and 1 mL/L H₃PO₄ at 30 °C with different concentrations of MSA

temperature effectively raises the number of active sites of electrode surface and, facilitates more nucleation sites and number [31,32]. Additionally,

increasing solution temperature expected to enhance transfer and diffusion of the deposition-related species [33,34]. The non-dimensional

$(J/J_m)^2-t/t_m$ curves (Figs. 9(b–f)) are closer to the theoretical model of instantaneous nucleation, indicating that on the whole, the nucleation and growth mode of the Pb deposition in the test system seems unchanged with temperature.

To address the issue that a barrier PbO_2 film formed on the anode of MPR, YANG et al [35] adopted the phosphoric acid (H_3PO_4) to effectively inhibit growth of the inert substance, ensuring a stable operation of the anodic process of MPR. In view of none report of the effect of H_3PO_4 on the cathodic process of MPR, we performed the present

research (Fig. 10). The linear sweep voltammetry (Fig. 10(a)) and $J-t$ transient (Fig. 10(b)) show that as the concentration of H_3PO_4 increases, the trend and shape of the curves are basically the same, indicating its little influence on the cathodic Pb deposition of MPR. Figures 10(c–f) present the non-dimensional $(J/J_m)^2-t/t_m$ curves, which are closer to the theoretical model of instantaneous nucleation, suggesting that the nucleation and growth mode of the Pb deposition in the test system is nearly unchanged with varying H_3PO_4 concentration from 0 to 3 mL/L.

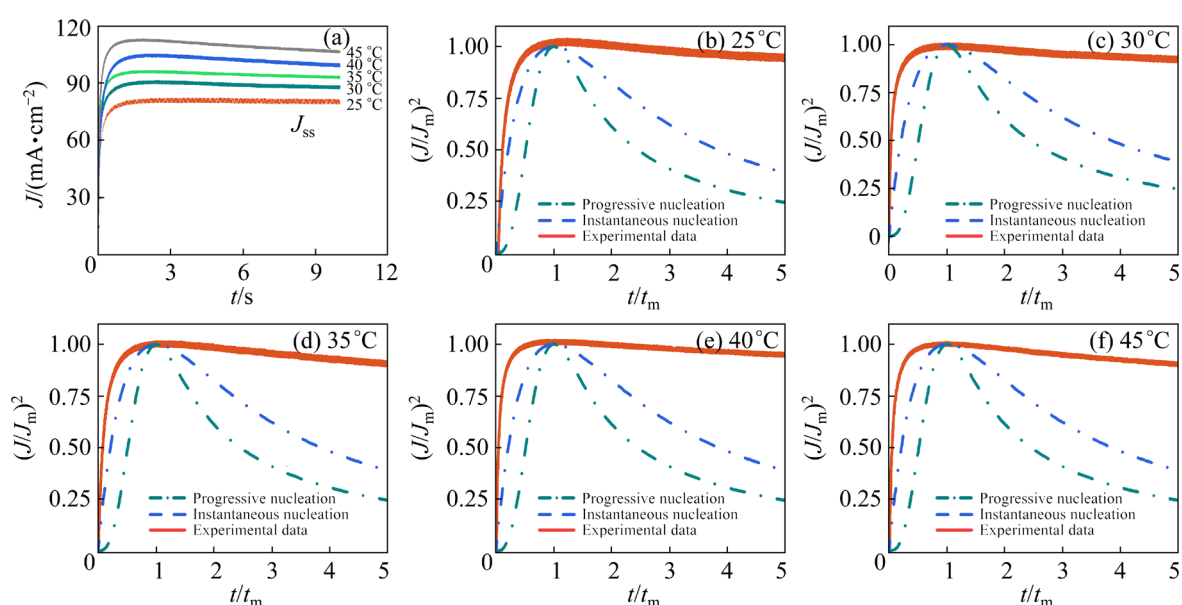


Fig. 9 $J-t$ (a) and $(J/J_m)^2-t/t_m$ (b–f) plots for Pb electro-deposition in solution containing 50 mol/L MSA, 150 g/L Pb^{2+} and 1 mL/L H_3PO_4 at different temperatures

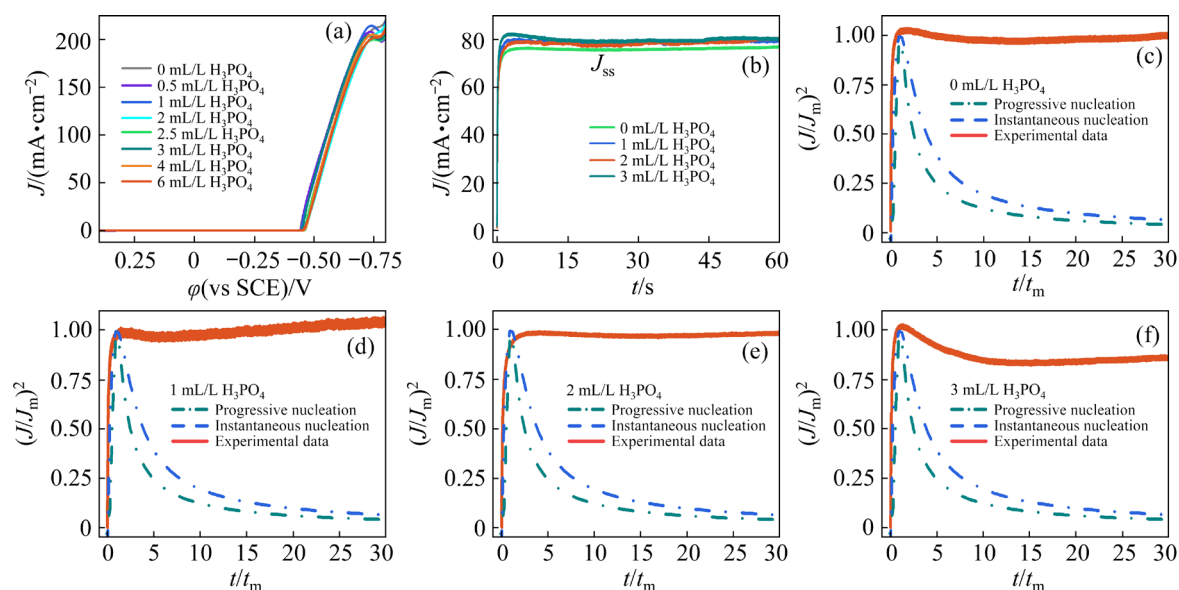


Fig. 10 Linear sweep voltammetry (a), $J-t$ (b) and $(J/J_m)^2-t/t_m$ (c–f) plots for Pb electrodeposition in solution containing 50 mol/L MSA and 150 g/L Pb^{2+} at 30 °C with different H_3PO_4 concentrations

3.2 Proof-of-concept operation of MPR

To demonstrate the feasibility of MPR process, we performed its bench-scale proof-of-concept operation. Figures 11(a) and (b) show the photograph and SEM observations of cathodic deposit of MPR process with addition of 2 g/L gelatin (GE) or 1 g/L sodium lignosulfonate (SL), respectively. Under photograph observation, the deposit, in the MSA system with GE, is smooth with fine dendrites at the edge, while in the MSA system with SL, it is also smooth but with no obvious dendrites at the edge and with excellent metal luster. Under SEM observations, the deposit in the MSA system with SL is denser than that in the MSA system with GE. Therefore, the MSA system with SL can achieve smooth and compact deposit with excellent metal luster. Figure 11(c) shows the current efficiency and energy consumption of Pb electro-refining in the MSA and H_2SiF_6 systems. The MSA system with GE achieves energy consumption of $94.98 \text{ kW}\cdot\text{h/t}$ Pb with current efficiency of 98.34%, while the MSA system with SL achieves energy consumption of $104.22 \text{ kW}\cdot\text{h/t}$ Pb with current efficiency of 99.24%. They are competitive with the H_2SiF_6 system with GE/SL, which requires energy consumption of $120 \text{ kW}\cdot\text{h/t}$ Pb with current efficiency of 95% [36]. Table 4 shows Pb purity of 99.9925% for the

deposit sample in the MSA system with SL, which satisfies the Pb purity standard of Pb ingot (GB/T 469—2013) of 99.97%. Overall, the MSA system can achieve efficient operation of the Pb electro-refining with high-quality Pb product, which would advance it towards industrial application. The performance of MPR would be further improved by the low-investment micro-kinetics modelling design [37–39].

Table 4 Chemical composition of cathodic deposits (wt.%)

Pb	Sn	Zn	As	Sb
99.9925	0.001	0.0005	0.0009	0.0017
Bi	Fe	Ag	Cu	
0.0015	0.0004	0.0009	0.0002	

4 Conclusions

(1) The cyclic voltammetry results revealed that the Pb deposition of MPR underwent a process of nucleation and growth through a redox reaction of Pb^{2+}/Pb , which was irreversible with diffusion step as the controlled one.

(2) The CA results indicated that the current density initially increased to maximum values due to the formation and growth of crystal nuclei, and subsequently decreased due to the overlap of growth centers, namely, the disappearance of growth centers and the regeneration of new growth centers. This phenomenon agreed well with the characteristic of the three-dimensional nucleation mode.

(3) The nucleation and growth mode of the deposition of MPR was closer to the characteristic of instantaneous nucleation, despite variations of the Pb^{2+} concentration, MSA concentration and temperature.

(4) The bench-scale operation of MPR process achieved energy consumption of $104.22 \text{ kW}\cdot\text{h/t}$ Pb and current efficiency of 99.24%, which was competitive with the energy consumption of $120 \text{ kW}\cdot\text{h/t}$ Pb and current efficiency of 95% for H_2SiF_6 system.

(5) A smooth and compact deposit in Pb purity of 99.9925% was obtained, which satisfied the purity standard of Pb ingot (GB/T 469—2013) of 99.97%.

(6) The anodic process of MPR, especially its

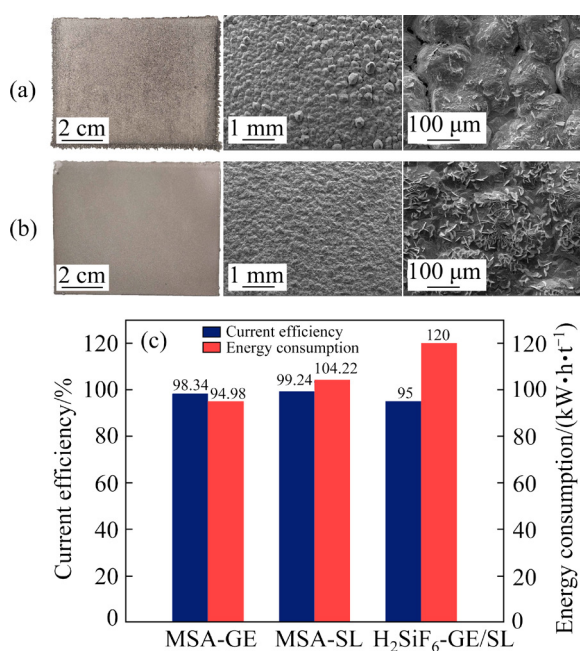


Fig. 11 Morphology of cathodic deposits (a, b) and energy consumption and current efficiency (c) during bench-scale operation of MPR

anodic dissolution, its anodic slime and material flow, would be investigated, to clarify its electrochemical behavior and adjusting mechanism. Also, the performance of MPR would be experimentally optimized by improving its solvent formulation.

Acknowledgments

This research is supported by BASF New Material Pb Methanesulfonic Acid System Pb Electrolytic Refining Project, China (No.738010278), and the Natural Science Foundation of Hunan Province of China for Youths (No. 2020JJ5628).

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甲基磺酸体系粗铅电解精炼的电沉积行为与概念验证运行

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摘要: 提出一种替代传统氟硅酸体系的甲基磺酸(MSA)体系, 它具有挥发性低、腐蚀性低、热稳定性良好和导电性高的优点, 能够实现绿色高效铅电解精炼。探讨基于 MSA 体系的粗铅电精炼(MPR)电沉积行为, 包括其运行机理、反应可逆性、形核和生长模式。基于循环伏安法(CV)和计时电流法(CA), 揭示受扩散控制且不可逆的MPR 铅沉积过程, 建立MPR 铅沉积形核和生长的瞬态成核理论模型。MPR 小规模验证性运行实现了 104.22 kW·h/t Pb 的能耗和 99.24% 的电流效率, 相较于 H₂SiF₆ 体系的 120 kW·h/t Pb 能耗与 95% 电流效率, 具有竞争性。MPR 小规模运行获得了纯度 99.9925% 且光滑致密的铅沉积层, 满足铅锭纯度 99.97% 的标准(GB/T 469—2013)。

关键词: 铅电解精炼; 甲基磺酸; 电沉积行为; 电化学分析; 阴极形貌

(Edited by Xiang-qun LI)