



# A simple modeling study of the Ce(IV) regeneration in sulfuric acid solutions

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## ABSTRACT

The electrochemical regeneration of Ce(IV) for mediated electrochemical oxidation in sulfuric acid media was investigated in an electrolytic membrane reactor. A simple kinetic model was developed to analyze and simulate the regeneration of Ce(IV) in the electrolysis process. The model was based on the Faraday's law and the mass balance of components in the reactor. The key operating conditions of the initial electrolyte concentration and the regeneration time were analyzed. It was found that the simulating model agreed well with the experimental data for regeneration of Ce(IV). Experimental results showed that  $\text{Ce}(\text{SO}_4)_2$  is the active species. The decomposition of surface complex of Ce(IV) at the anode surface is the rate determining step. Constant-current electrolysis shows that the high proton and Ce(III) concentrations are electrochemically favorable for the regeneration of Ce(IV). The current efficiency for regeneration of Ce(IV) decrease obviously with the increase of  $\text{SO}_4^{2-}$  concentration from 0.8 to 2.4 mol/L.

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## 1. Introduction

In recent decades, environmental pollution has become a global problem. The introduction of more stringent pollution regulations, coupled with financial and social pressures for sustainable development, has pressed to research and develop new and more efficient pollutant treatment technologies. The application of electrochemical oxidation methods for the treatment of pollutants has been attracted much more interest since it uses a clean reagent 'the electron'. The methods can be employed in oxidation of many different types of organic substrates [1–15], recirculation of spent Cr-etching solutions containing high concentrations of Cr(III) [16,17], removal of hydrogen sulfide from the atmosphere [18], removal of  $\text{SO}_2$  and  $\text{NO}_x$  from waste gases [19]. The electrochemical treatment of organic and inorganic substrates could be carried out by direct electrochemical oxidation (DEO) or mediated electrochemical oxidation (MEO), such as the degradation of phenol [1,3–5],  $\beta$ -dicarbonyl [6], aromatic derivatives [7], EDTA [10,11], pesticides [15] and removal of  $\text{H}_2\text{S}/\text{NO}_2$  [18,19].

The disadvantage of the DEO processes is its low current efficiency: it is often impossible to make the anode reaction complete; the other disadvantage of the DEO processes is the reduced mass transfer of the pollutant from the bulk solution to the anode surface. In the MEO processes, the pollutant is destructed in the bulk solution by a mediate metal ion in the higher oxidation state. After the oxidation of the pollutant, the reduced mediate metal ion is

reoxidized in situ at the anode and thus cycled infinitely. MEO is one of the most promising technologies for the destruction of the pollutant. In MEO processes, the metal ion in acid media is oxidized from its lower oxidation state to higher oxidation state and this oxidized species destructs the pollutant compounds, meanwhile, the higher oxidation of the metal ion is reduced to the lower oxidation by the pollutant compounds. Therefore, the metal ion acts as a powerful oxidant and destructs the pollutant. Cerium (IV) has often been selected as a well-known redox mediator for it has high redox potential and negligible rate of water oxidation comparing to silver and cobalt, and also cerium can be recovered and reused without much loss. Cerium belongs to the light lanthanoids and is about 100 times more abundant than cadmium in the earth's crust. Cerium is used in a variety of industrial fields as catalysts, lighters, glass additives, ceramics, magnets and abrasives, solar cells, fuel cells, phosphor/luminescence, gas sensors, oxygen pumps, and metallurgical and glass/ceramic applications. The wild usage of cerium as redox mediator is not only because their effectiveness but also due to the null toxicity for most of them [20]. The toxicity of the chemical products is classified according to the parameter lethal dose 50 (LD50). As an indicative result, lanthanide chlorides exhibit values for the LD50 similar to the sodium salt [21]. The kinetic and mechanistic of the oxidation of the pollutant by Ce(IV) in aqueous  $\text{H}_2\text{SO}_4$  media have been extensively studied [22–27].

There is one common problem in using Ce(IV) to destruct different pollutants in MEO processes, which is the effective way of Ce(IV) regeneration. The factors involved in the regeneration of Ce(IV) influence the anodic mechanism of oxidizing Ce(III) to Ce(IV). However, the electrochemical processes of the regeneration of Ce(IV) on  $\text{PbO}_2$  electrode are not completely understood yet because of

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discrepancies concerning the influence of variable parameters on the degradation rate of the pollutant. Since effective and economical means of the treatment of pollutants requires the appropriate electrolysis conditions, it is necessary to optimize the regeneration conditions of Ce(IV), and to establish the relationship between the partial current efficiency and the applied current density, concentrations of Ce(III), H<sup>+</sup> and sulfate ion in the filterpress-type cell. For these purposes, we have established the relationship between anode current density and concentrations of cerium (III), H<sup>+</sup>, sulfate ion, and regeneration time.

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Reagents

Cerium (III) carbonate (99.99%, Terio Corporation, China), sulfuric acid (analytical reagent, China), magnesium sulfate (analytical reagent, China) were used without further purification. Cerium (III) sulfate was prepared by dissolution of cerium (III) carbonate in sulfuric acid and diluted to the desired concentration with doubly distilled water. Cerium (III) sulfate was titrated against a standard solution of EDTA, using methyl orange as an indicator. Concentration of Ce(IV) was titrated with ferrous ammonium sulfate using ferroin 1.10-phenanthroline-iron(II) as indicator. All other chemicals used were either analytical grade or chemically pure substances.

#### 2.1.2. Anion-exchange membrane

The PE-203 (Shanghai Qjulong Chemical Co., Ltd.) was employed as an anion exchange membrane with polyethylene as substrate, RN<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub> as functional ion, exchange capacity of 2 ± 0.2 mequiv./g (dry membrane), water content of about 35%, resistance of about ≤4.5 Ω/cm<sup>2</sup>, thickness of about 0.3 mm and selectivity of 96%. The membrane was equilibrated with sulfuric acid solution of 0.5 mol/L for one night and then rinsed with double distilled water before use.

#### 2.1.3. Anode

The electrodeposition of PbO<sub>2</sub> on Ti/RuO<sub>2</sub> has been carried out in an electrochemical cell filled with a 0.5 M Pb(NO<sub>3</sub>)<sub>2</sub> and 2.5 M HNO<sub>3</sub> solution at 65 °C [28]. The anode was a titanium mesh coated with a thin film of RuO<sub>2</sub>. The electrodeposition of PbO<sub>2</sub> was performed for 3 h, and β-PbO<sub>2</sub> is formed. The average mass of PbO<sub>2</sub> was 0.25 g/cm<sup>2</sup>. The obtained deposit was mat grey, adherent, regular and uniform.

### 2.2. Methods

#### 2.2.1. Electrochemical membrane reactor

The electrochemical oxidation of Ce(III) was carried out in a filterpress-type cell which was fabricated in our laboratory. This system featured an electrolytic membrane reactor, two storage tanks, two magnetic pumps and an adjustable DC power supply. PbO<sub>2</sub> was used as the anode, made of titanium plate coated with PbO<sub>2</sub> (Shanxi Elade New Material Technology Co., Ltd. China). Copper mesh was used as the cathode. Both the apparent geometrical surface areas of electrodes are of 100 mm × 115 mm (effective surface areas: 115 cm<sup>2</sup>). The anode and cathode were separated by an anion exchange membrane. The anode and cathode compartments of the cell were coupled to the anolyte and catholyte vessels respectively. The DC current (WYK-3020 constant current regulator, 0–20 A, 0–30 V) was applied to the reactor, and the cell voltage was recorded at regular intervals. The solutions were circulated through the anodic and cathodic compartments continuously at a given flow rate using magnetic pumps. The temperature of the electrolyte was controlled to 25 °C with a variation of ±1 °C using a

thermostatic control. All experiments were performed under constant current.

### 2.3. Data processing

During the experimental process, samples were collected at specified time intervals. Concentrations of Ce(IV) and Ce(III) were checked by redox titration with standard ferrous sulfate solution and EDTA respectively. From the concentrations of Ce(IV) and Ce(III), the current efficiencies of the anode and the conversion rate of Ce(III) to Ce(IV) were calculated. All current densities relate to the apparent surface areas of the electrodes. The current efficiencies were calculated using Eq. (1), which yield the ratio between the current effectively used for the Ce(III) oxidation to Ce(IV) and the total current supplied.

$$\eta_a = \frac{100 z F V_a}{M_{Ce} I_{app} A_a} \left( \frac{\Delta C_{Ce}}{\Delta t} \right) \quad (1)$$

where:  $\eta_a$  is the anode current efficiencies expressed as percentages,  $\Delta C_{Ce}/\Delta t$  is the concentration drop for cerium (III) in the time interval  $\Delta t$  (g dm<sup>-3</sup> s<sup>-1</sup>),  $z$  are the number of electrons used in the electrolytic reactions ( $z=1$  for oxidation of Ce(III) to Ce(IV)),  $F$  is the Faraday constant (96487 A s mol<sup>-1</sup>),  $V_a$  is the volume of anolyte (L),  $A_a$  is the effective anode area (m<sup>2</sup>),  $I_{app}$  is the applied current density (A/m<sup>2</sup>),  $M_{Ce}$  is the molar mass (140.12 g/mol for cerium).

The partial current densities ( $I_{Ce}$ ) used for the Ce(III) oxidation to Ce(IV) were calculated using Eq. (2),

$$I_{Ce} = \eta_a I_{app} \quad (2)$$

### 2.4. The electrolysis process

The cathode compartment was filled with a sulfuric acid solution of 1.0 mol/L, and the anode compartment contained a solution of different concentrations of H<sub>2</sub>SO<sub>4</sub> and Ce(III) sulfate. The unlacquered face of the cathode was polished with fine silicon carbide paper and rinsed with double distilled water and acetone. The anode and cathode were activated together in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at selected constant current density until the cell voltage became stable. The anode and cathode were placed at a constant distance of 1.5 mm from the anion exchange membrane. The cell voltage was recorded at regular intervals. During the oxidation process, the anolyte and catholyte were recycled with a magnetic pump at the flow rate of 0.23 m/s. The anode current efficiency was calculated from the concentration of cerium (IV). The effects of concentration of Ce(III), SO<sub>4</sub><sup>2-</sup>, H<sup>+</sup> and anode current density on the partial current efficiency were studied.

## 3. Results and discussion

### 3.1. Effect of different operating factors on current efficiency for the regeneration of Ce(IV)

The electro-regeneration of Ce(IV) involves four main electrode reactions, and sulfate ions migrate through the anion exchange membrane under an electric field. Ce(III) is oxidized at the anode and H<sup>+</sup> is reduced at the cathode, while SO<sub>4</sub><sup>2-</sup> permeates mainly through the anion exchange membrane from the cathode chamber to the anode chamber to balance charge.

The electro-regeneration of Ce(IV) and reduction of H<sup>+</sup> in the anion exchange membrane reactor, the main reactions and their standard electrode potentials ( $E^\theta$ ) vs. standard hydrogen electrode are as follows:

At the cathode:



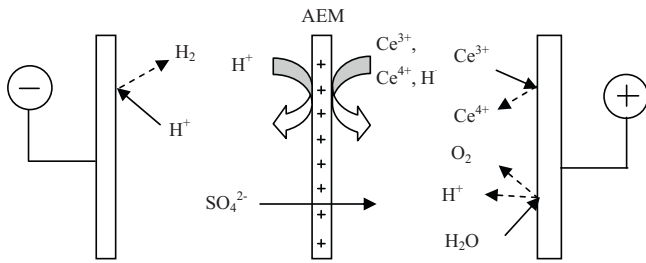
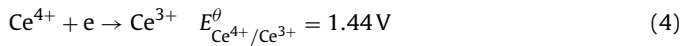
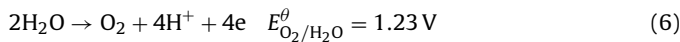
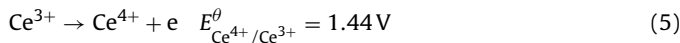


Fig. 1. Schematic representation of electrochemical cell setup.



At the anode



The overall electrochemical reaction is the sum of Reactions (3) and (5) plus sulfate ions



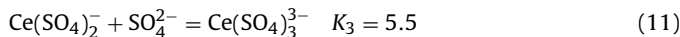
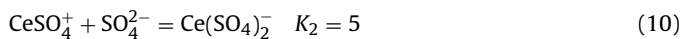
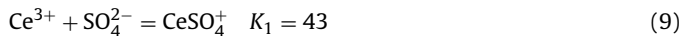
Reactions (3) and (5) are the main reactions, while reactions (4) and (6) are the undesirable side reactions, and reaction (4) can be neglected due to the selective permeation of the anion exchange membrane for anion as shown in Fig. 1.

The concentrations of Ce(III) and Ce(IV) comply with conservation of mass relationship



The conductivity of electrolytes were not affected by composition and flow rate of electrolyte due to the presence of a large number of supporting electrolytes; and the activity of anode surface at the same current density remained unchanged.

Both cerium (III) and cerium (IV) are very labile species; ligands are exchanged in the microseconds time scale. In the presence of sulfate ions, H<sub>2</sub>O molecules in the inner coordination sphere of cerium at both oxidation states are substituted. In the sulfuric acid media, the stepwise stability constants and suitable equilibriums for aqueous Ce(III)–sulfate systems are as follows [29,30]



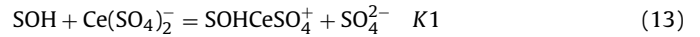
Previous studies indicated that Ce(III) exists predominantly as free metallic ion Ce<sup>3+</sup> when the concentration of SO<sub>4</sub><sup>2-</sup> is lower than 0.5 M and mainly as complex ions CeSO<sub>4</sub><sup>+</sup> and/or Ce(SO<sub>4</sub>)<sub>2</sub><sup>-</sup> when the concentration of SO<sub>4</sub><sup>2-</sup> is greater than 0.5 M. In our experiments, the concentration of sulfate ions ranged between 0.8 and 2.4 mol/L, therefore, we can assume that the predominant active ion participating in the anode oxidation was Ce(SO<sub>4</sub>)<sub>2</sub><sup>-</sup>, while the main form of tetravalent cerium is Ce(SO<sub>4</sub>)<sub>3</sub><sup>3-</sup> [31,32]

Over the past several decades, many researchers have indicated that the metal oxides could be hydroxylated by H<sub>2</sub>O to form surface OH groups and release H<sup>+</sup>; metal cations can adsorb onto these surfaces and form surface complexations [33,34]. As for PbO<sub>2</sub> anode, Pavlov and co-workers [35,36] proposed that water may react at the inter-crystalline surface of PbO<sub>2</sub> to form surface OH ions, according to the following reaction.



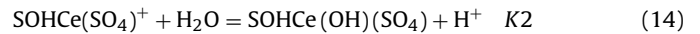
Pb\*O(OH)<sub>2</sub> is an active center located in the hydrous layer.

Since the oxidation of Ce(III) was the redox reaction to produce Ce(IV), only the formation of surface complexes of Ce(III) was considered. On the active center of hydroxylated surface of PbO<sub>2</sub>, the formation of surface complexation of Ce(III) [37–41] at the surface functional ions can occur according to

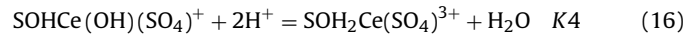
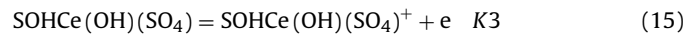


where S and OH is the representative of the surface of anode and hydroxyl ions respectively. SOH is the active center of hydroxylated surface of anode, SOHCeSO<sub>4</sub><sup>+</sup> is the surface complexation of Ce(III).

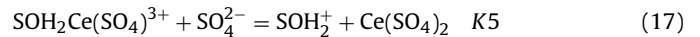
Previous studies [42–44] have shown that pH value of hydroxylated surface of PbO<sub>2</sub> can be expected to reach a value of 9.34 when a positive potential is applied to anode. Under this condition, the surface of cerium complexes could be further hydrolyzed to form complexes SOHCe(OH)(SO<sub>4</sub>) as following



When current passes through the electrolytic cell, upon anodic polarization, an electrochemical reaction occurs as following



And then the surface complexes decompose as following



Suppose (17) is the determining step, the decomposition of the surface complex SOH<sub>2</sub>Ce(SO<sub>4</sub>)<sup>3+</sup> is the key process for the oxidation of cerium (III). The electrolytic oxidation of Ce(III) is not reversible electrode reactions for high anodic potential, so the reduction reaction of Ce(IV) is negligible. The concentration of SOH<sub>2</sub>Ce(SO<sub>4</sub>)<sup>3+</sup> can be derived from (10) to (16) as following

$$c_r = \frac{K_1 K_2 K_3 K_4 c_{\text{SOH}} c_{\text{Ce}^{3+}} c_{\text{H}^+}}{c_{\text{SO}_4^{2-}}} \quad (19)$$

where, c<sub>SOH</sub>, c<sub>Ce<sup>3+</sup></sub>, c<sub>SO<sub>4</sub><sup>2-</sup></sub> and c<sub>H<sup>+</sup></sub> is concentration of SOH, Ce<sup>3+</sup>, SO<sub>4</sub><sup>2-</sup> and H<sup>+</sup>.

In the electrolytic oxidation process, the electrolyte passed through the anode compartment in the form of plug flow. In each cycle of the electrolyte, the reactive concentration of Ce(III) is c<sub>r</sub> = c<sub>in</sub> – c<sub>out</sub>. The concentration of SOH<sub>2</sub>Ce(SO<sub>4</sub>)<sup>3+</sup> participating in oxidation reaction is equal to c<sub>r</sub>. Where, c<sub>in</sub> and c<sub>out</sub> is inlet and output concentration of Ce(III)

The intermittent recirculation was applied in the actual process of the regeneration of Ce(III), the output concentration of Ce(III) was a function of time. The relationship between concentration and time was obtained as Eq. (20)

$$V_T \frac{dc_{(\text{in})}}{dt} = Qc_r \quad (20)$$

where, V<sub>T</sub> (m<sup>3</sup>) and Q (m<sup>3</sup>/s) is the total volume and flow rate of anolyte, respectively.

The residence time of electrolyte in the anode compartment is τ = V<sub>T</sub>/Q, the output concentration of Ce(III) is Eq. (21)

$$c_{(\text{rin},t)} = c_{(\text{rin},0)} \exp \left[ -\frac{k_m S}{V_T} t \right] \quad (21)$$

where c<sub>(rin,t)</sub> and c<sub>(rin,0)</sub> is the output and inlet concentration of SOH<sub>2</sub>Ce(SO<sub>4</sub>)<sup>3+</sup> (mol/L), k<sub>m</sub> is the rate coefficient, S is the cross-sectional area of the anode compartment (m<sup>2</sup>)

According to Faraday's law, the partial current i<sub>Ce</sub> was obtained as following

$$i_{\text{Ce}} = Fc_{(\text{rin},t)} = Fc_{(\text{rin},0)} \exp \left[ -\frac{k_m S}{V_T} t \right] \quad (22)$$

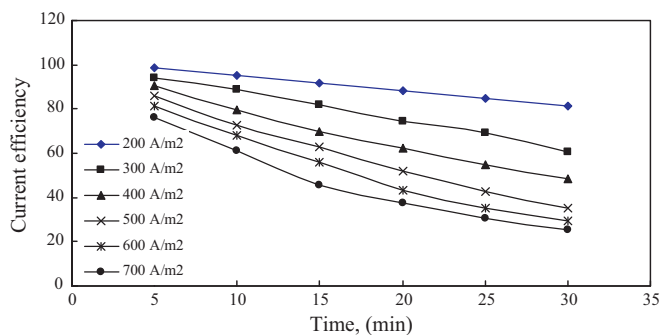


Fig. 2. current efficiency vs. time at different current density.

The partial current  $i_{Ce}$  is the number of charges that in unit time cross the unit cross-sectional area due to the oxidation of  $\text{SOH}\text{Ce}(\text{OH})\text{SO}_4$ . In each cycle of the electrolyte, the reactive concentration of  $\text{Ce}(\text{III})$  is  $c_r = c_{\text{in}} - c_{\text{out}}$ . The concentration of  $\text{SOH}_2\text{Ce}(\text{SO}_4)^{3+}$  participating in oxidation reaction is equal to  $c_r$ . The output concentration of  $\text{SOH}_2\text{Ce}(\text{SO}_4)^{3+}$  therefore is equal to  $c_{\text{rin},t}$ . Substituting Eq. (19) into Eq. (22), that is,

$$i_{Ce} = Fc_{\text{rin},t} = Fc_r = F \frac{K_1 K_2 K_3 K_4 c_{\text{SOH}} c_{\text{Ce}^{3+}} c_{\text{H}^+}}{c_{\text{SO}_4^{2-}}} \exp \left[ -\frac{k_m S}{V_T} t \right] \quad (23)$$

Under certain electrolytic conditions, anode surface properties and its active surface areas remain unchanged; consider that  $c_{\text{SOH}}$  is constant and the partial current density from the Eq. (23) was obtained as following

$$I_{Ce} = Fc_r = F \frac{K_1 K_2 K_3 K_4 c_{\text{SOH}} c_{\text{Ce}^{3+}} c_{\text{H}^+}}{c_{\text{SO}_4^{2-}} S_a} \exp \left[ -\frac{k_m S}{V_T} t \right] \quad (24)$$

$$I_{Ce} = I_{\text{app}} \leftarrow \eta = Fk \frac{c_{\text{SOH}} c_{\text{Ce}^{3+}} c_{\text{H}^+}}{c_{\text{SO}_4^{2-}}} \exp \left[ -\frac{k_m S}{V_T} t \right] \quad (25)$$

where,  $k = \frac{K_1 K_2 K_3 K_4}{S_a}$ ,  $I_{Ce}$  and  $I_{\text{app}}$  is the partial and the applied current density ( $\text{A}/\text{m}^2$ ) through the electrolytic cell,  $\eta$  and  $S_a$  is the current efficiency (%) and the active anode surface area ( $\text{m}^2$ ).

Eq. (25) shows that the partial current density has the linear relationship with  $c_{\text{Ce}^{3+}}$ ,  $\left( c_{\text{SO}_4^{2-}} \right)^{-1}$  and  $c_{\text{H}^+}$  respectively. And it has logarithmic relationship with regeneration time.

To verify the correctness of the above reaction mechanism, we conducted the experiments to test the effects of the regeneration time and electrolysis parameters on current efficiency.

### 3.2. Effect of regeneration time on partial current efficiency at different current density

The effect of current density was studied in the range of 200–700  $\text{A}/\text{m}^2$  with fixed initial  $\text{H}^+$  concentration of 3.0 mol/L related to sulfuric acid in the catholyte. The anolyte contained  $\text{H}^+$  of 1 mol/L and  $\text{CeO}_2$  of 14.92 g/L. The results are shown in Fig. 2. Fig. 2 shows that current efficiency gradually decreases with time and it increases with decreasing current density.

As it can be seen, with an increase in current density from 200 to 700  $\text{A}/\text{m}^2$ , the current efficiency decreased at the same electrolysis time. Meanwhile, the current efficiency decreased with time at different current density. These decreases can be attributed to the decrease in the concentration of  $\text{Ce}(\text{III})$ . The current density was higher, the concentration of  $\text{Ce}(\text{III})$  decreased more rapidly. As both water and  $\text{Ce}(\text{III})$  can be oxidized at the anode, the oxygen evolution rate is high, and the oxidation rate of  $\text{Ce}(\text{III})$  appears to be low.

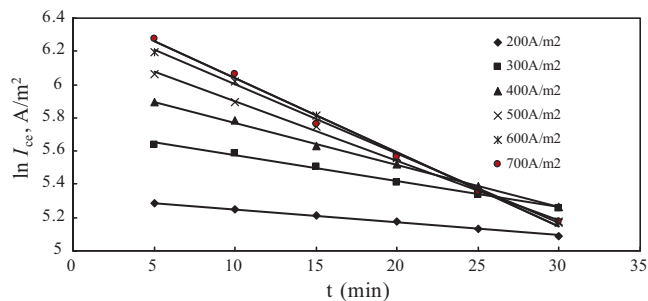


Fig. 3. Plot of  $\ln I_{Ce}$  vs. time at variation of current densities.

From the data shown in Fig. 2, the  $\ln I_{Ce}$  vs. time at different current density can be deduced. The results were plotted in Fig. 3.

Fig. 3 shows that the logarithm of the partial current density for oxidation of  $\text{Ce}(\text{III})$  and regeneration time has a linear relationship at different current densities. This result is consistent well with the Eq. (25). It also can be seen that the partial current efficiency decreases more sharply with increasing current density due to the conversion of  $\text{Ce}(\text{III})$  to  $\text{Ce}(\text{IV})$  more rapid with time for a higher constant current electrolysis. Fig. 3 also showed that the intercept of each line is different at different current densities, that is  $Fk c_{\text{SOH}} c_{\text{Ce}^{3+}} c_{\text{SO}_4^{2-}} c_{\text{H}^+}$  is variable with the current density.

If the initial concentration of  $c_{\text{H}^+}$ ,  $c_{\text{Ce}^{3+}}$  and  $c_{\text{SO}_4^{2-}}$  in the catholyte is fixed, we can obtain Eq. (26) from Eq. (25)

$$\ln I_{Ce} = \ln k_1 c_{\text{SOH}} - \frac{k_m S}{V_T} t \quad (26)$$

where  $k_1 = \ln Fk \frac{c_{\text{Ce}^{3+}} c_{\text{H}^+}}{c_{\text{SO}_4^{2-}}}$ . As  $t = 0$ , we obtain Eq. (27)

$$\ln I_{Ce} = \ln k_1 c_{\text{SOH}} \quad (27)$$

$\ln k_1 c_{\text{SOH}}$  is equal to the intercept of line shown in Fig. 3.

Eq. (27) shows that the logarithm of partial current density and the intercepts of lines shown in Fig. 3 has linear relationship. The results are shown in Fig. 4. As current density reached up to 700  $\text{A}/\text{m}^2$ , the intercept is below normal. As can be seen from Fig. 4, the intercept increases linearly with the increase of current density from 200 to 600  $\text{A}/\text{m}^2$ . This result reveals that the concentration of SOH was improved linearly when the current density was increased from 200 to 600  $\text{A}/\text{m}^2$ . This result reveals that the concentration of SOH was improved linearly when the current density was increased from 200 to 600  $\text{A}/\text{m}^2$ . From Fig. 4, it is clear that the  $\ln k_1 c_{\text{SOH}}$  at current density of 600  $\text{A}/\text{m}^2$  is close to that at current density of 700  $\text{A}/\text{m}^2$ . For  $k_1$  is the constant as concentrations of  $\text{Ce}(\text{III})$ ,  $\text{H}^+$  and  $\text{SO}_4^{2-}$  were fixed, the concentration of SOH at current density of 600  $\text{A}/\text{m}^2$  is close to that at current density of 700  $\text{A}/\text{m}^2$ . This result indicated that the concentration of SOH was close to a saturation

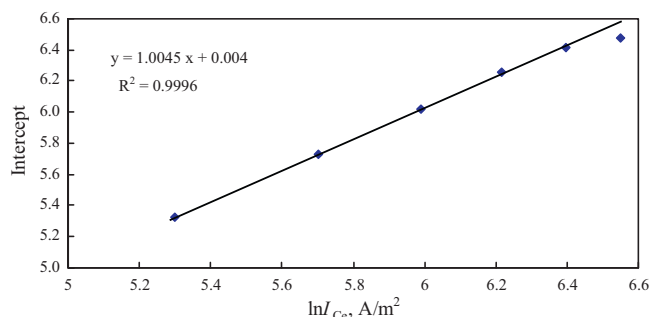
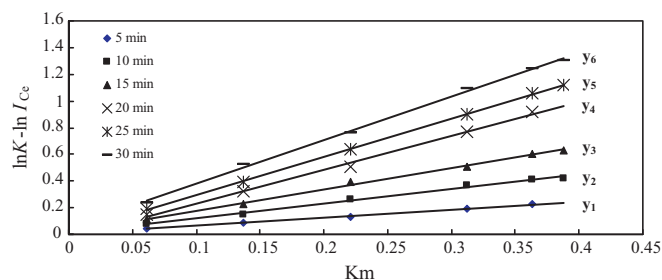


Fig. 4. The linear relationship between the logarithm of current density and the intercepts.



**Fig. 5.**  $\ln K - \ln I_{Ce}$  vs.  $k_m$ .  $y_1 = 0.605x_1 + 0.0047$ ,  $R_2 = 0.9967$ ;  $y_2 = 1.005x_2 + 0.0083$ ,  $R_2 = 0.9936$ ;  $y_3 = 1.5879x_3 + 0.0198$ ,  $R_2 = 0.9962$ ;  $y_4 = 2.5260x_4 + 0.0208$ ,  $R_2 = 0.9956$ ;  $y_5 = 2.8732x_5 + 0.007$ ,  $R_2 = 0.9997$ ;  $y_6 = 3.2608x_6 + 0.055$ ,  $R_2 = 0.9978$ .

concentration when current density was enhanced up to  $600 \text{ A/m}^2$ . The  $\ln k_1 c_{SOH}$  at current density of  $700 \text{ A/m}^2$  cannot increase linearly and it was lower than the normal value. Therefore, the increase of current density higher than  $700 \text{ A/m}^2$  had no more benefit to raise the concentration of SOH.

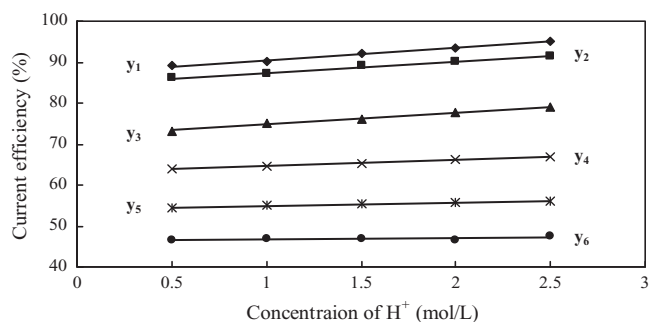
The increase in concentration of active center of hydroxylated surface of anode with increasing current density will improve rate coefficient ( $k_m$ ). From Eq. (26), we can rearrange equation as

$$\ln K - \ln I_{Ce} = \frac{S \llcorner \rightarrow t}{V_T} k_m$$

where  $K$  is  $k_1 c_{SOH}$ . As  $S$ ,  $V_T$  and  $t$  is fixed,  $\ln K - \ln I_{Ce}$  and  $k_m$  has a linear relationship. The results deduced from Fig. 2 are shown in Fig. 4. Fig. 4 shows that  $k_m$  varies with current density (Fig. 5).

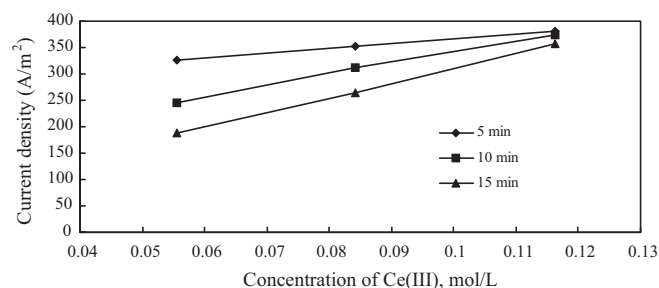
### 3.3. Effect of concentration of $H^+$ in the anolyte on partial current efficiency

Electrolysis was conducted by varying the concentration of  $H^+$  from  $0.5 \text{ mol/L}$  to  $2.5 \text{ mol/L}$  in the presence of  $0.0921 \text{ mol/L}$  of  $Ce(III)$  at temperature of  $25^\circ\text{C}$ , and current density of  $300 \text{ A/m}^2$ . Each anolyte sample contained  $1.25 \text{ mol/L}$  sulfate ions adjusted with  $MgSO_4$  in double distilled water. The temperature was adjusted to  $25^\circ\text{C}$ , and electro-oxidation proceeded for 30 min. From Eq. (25), if concentrations of  $Ce(III)$  and  $SO_4^{2-}$  were fixed, and concentration of SOH kept at the same value as the current density applied was fixed, we can derive that current efficiency has linear relationship with concentration of  $H^+$  in the anolyte at constant current electrolysis. The results are plotted in Fig. 6. Fig. 6 shows that the relationship between current efficiency and concentration of  $H^+$  is consistent with the Eq. (25)



**Fig. 6.** Effect of concentration of  $H^+$  in the anolyte on the current efficiency for different operating time. (◆) 5 min, (■) 10 min, (▲) 15 min, (×) 20 min, (✕) 25 min, (●) 30 min.

$y_1 = 3.034x_1 + 87.377$ ,  $R_2 = 0.9946$ ;  $y_2 = 2.734x_2 + 84.695$ ,  $R_2 = 0.9938$ ;  $y_3 = 2.904x_3 + 71.896$ ,  $R_2 = 0.9964$ ;  $y_4 = 1.500x_4 + 63.08$ ,  $R_2 = 0.9985$ ;  $y_5 = 0.776x_5 + 54.138$ ,  $R_2 = 0.9940$ ;  $y_6 = 0.302x_6 + 46.449$ ,  $R_2 = 0.3295$ . Conditions:  $0.0921 \text{ mol/L}$  of  $Ce(III)$  at temperature of  $25^\circ\text{C}$ , and current density of  $300 \text{ A/m}^2$ . Each anolyte sample contained  $1.25 \text{ mol/L}$  sulfate radical.



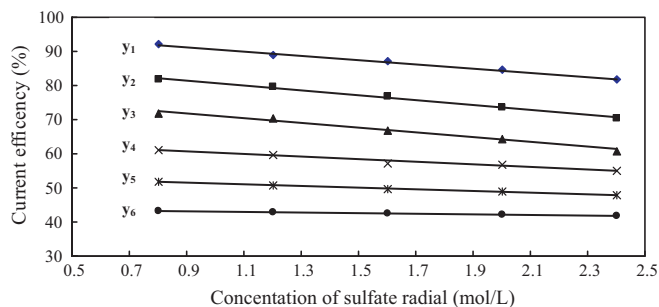
**Fig. 7.** Current density vs. initial concentration of  $Ce(III)$ . Conditions:  $1.0 \text{ mol/L}$  of  $H^+$  in the anolyte at temperature of  $35^\circ\text{C}$ , and current density of  $400 \text{ A/m}^2$ . Each anolyte sample contained  $1.0 \text{ mol/L}$  sulfate radical adjusted with  $MgSO_4$ .

### 3.4. Effect of initial concentration of $Ce(III)$ in the anolyte on partial current efficiency

The experiments were carried out with different initial  $Ce(III)$  concentrations ranging from  $0.05563$  to  $0.1162 \text{ mol/L}$  in the anolyte with the presence of  $1.0 \text{ mol/L}$  of  $H^+$  at temperature of  $35^\circ\text{C}$ , and current density of  $400 \text{ A/m}^2$ . Each anolyte sample contained  $1.0 \text{ mol/L}$  sulfate ions adjusted with  $MgSO_4$  in double distilled water. Fig. 7 shows the effect of the initial  $Ce(III)$  concentration on the partial current density. As is shown in Fig. 7, the partial current density increased linearly and significantly when the initial  $Ce(III)$  concentration in the anolyte increased at different regeneration time. This result revealed that the increase in initial concentration of  $Ce(III)$  helps to improve the current efficiency. The increase of the current efficiency with the increase of the concentration of  $Ce(III)$  can be deduced from Eq. (25). As concentrations of  $SO_4^{2-}$ ,  $H^+$ , and SOH were fixed, the  $I_{Ce}$  and concentration of  $Ce(III)$  has the linear relationship at the same electrolysis time. Because  $I_{Ce} = I_{app}\eta$ ,  $\eta$  will increase with the concentration of  $Ce(III)$  when  $I_{app}$  was fixed, that is to say, current efficiency will increase with the concentration of  $Ce(III)$  when  $I_{app}$  was fixed

### 3.5. Effect of initial concentration of sulfate ions in the anolyte on partial current efficiency

To verify the relationship between sulfate ions concentration and partial current efficiency, experiments were performed with sulfate ions concentration of  $0.8, 1.2, 1.6, 2.0$  and  $2.4 \text{ mol/L}$  at the current density of  $400 \text{ A/m}^2$ . The results are shown in Fig. 8. Fig. 8 shows that the partial current efficiency decreases linearly as the sulfate ions concentrations increasing. The increase of sulfate ions concentration has no benefit in improving current efficiency. This



**Fig. 8.** Current efficiency vs. concentration of sulfate ions at different time. (◆) 5 min, (■) 10 min, (▲) 15 min, (×) 20 min, (✕) 25 min, (●) 30 min.

$y_1 = -6.295x_1 + 96.974$ ,  $R_2 = 0.9955$ ;  $y_2 = -7.28x_2 + 88.11$ ,  $R_2 = 0.9944$ ;  $y_3 = -6.9125x_3 + 77.878$ ,  $R_2 = 0.9863$ ;  $y_4 = -3.7125x_4 + 63.88$ ,  $R_2 = 0.962$ ;  $y_5 = -2.3475x_5 + 53.548$ ,  $R_2 = 0.9948$ ;  $y_6 = -0.785x_6 + 43.678$ ,  $R_2 = 0.9958$ . Conditions:  $1.0 \text{ mol/L}$  of  $H^+$  in the anolyte at temperature of  $35^\circ\text{C}$ , and current density of  $400 \text{ A/m}^2$ ,  $0.0921 \text{ mol/L}$  of  $Ce(III)$  in each anolyte.

phenomenon, similar to that has been observed in other researches [17,28], was attributed to the strong complexation of sulfate ions with Ce(III). This change in concentration of Ce(III) active species [17] results in a lower current efficiency for the oxidation of Ce(III). When the concentration of sulfate ions increases from 0.8 mol/L to 2.4 mol/L, the partial current efficiency for regeneration of Ce(IV) dropped from 92% to 78% in 5 min. As the electrolysis carried out, the partial current efficiency gradually approaches to the same value. In 30 min, the partial current efficiency reduced to about 43%.

#### 4. Conclusions

In this research, the simple model of electrochemical regeneration of Ce(IV) in sulfuric acid solutions at PbO<sub>2</sub> anode has been developed, and the model was verified under different experimental conditions, i.e., different initial concentration of Ce(III), SO<sub>4</sub><sup>2-</sup> and H<sup>+</sup>. The experimental results reveal that the simulated model agreed with the experimental data for regeneration of Ce(IV) very well. Experimental results show that Ce(SO<sub>4</sub>)<sub>2</sub><sup>-</sup> is the kinetically active species. The decomposition of surface complex of Ce(IV) at the anode surface is the rate determining step. The activity of the lead dioxide electrode, corresponding to the oxidation of Ce(III), depends on the applied current density, in the range of 200 A/m<sup>2</sup> to 600 A/m<sup>2</sup>, PbO<sub>2</sub> anode activity linearly increases with the current density. Experimental results show that the logarithm of the partial current efficiency for regeneration of Ce(IV) decreases with the regeneration time, and higher proton and Ce(III) concentrations are electrochemically favorable for the regeneration of Ce(IV) and for the generation of high current efficiency in sulfuric acid media. In addition, the increase of sulfate ion concentration has a negative effect on the regeneration of Ce(IV), the partial current efficiency for regeneration of Ce(IV) visibly decreases with the increase of sulfate ion concentration from 0.8 to 2.4 mol/L.

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