

Anion effects on the electrochemical regeneration of Ce(IV) in nitric acid used for etching chromium

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Abstract

The anion impurities such as SO_4^{2-} , Cl^- , and $\text{Cr}_2\text{O}_7^{2-}$ commonly present in the spent (hazardous) Cr-etch solutions from color filter manufacturing processes may influence the solutions' regeneration by the electrooxidation of Ce(III) to Ce(IV). This study, therefore, investigated the effects of these anions on Ce(III)/Ce(IV) redox reactions at glassy carbon in HNO_3 . In cyclic voltammetric tests, the presence of SO_4^{2-} decreased the formal potential but increased the peak potential separation (ΔE_p) of Ce(III)/Ce(IV) couple, and lowered the peak current for Ce(IV) reduction whereas Cl^- did not change the formal potential and ΔE_p , but the peaks for Cl^- and Ce(III) oxidation partially overlapped. $\text{Cr}_2\text{O}_7^{2-}$ slightly lowered the peak current for Ce(III) oxidation but significantly decreased that for Ce(IV) reduction. The Tafel slope for Ce(III) oxidation was $\sim 65 \text{ mV decade}^{-1}$ in the absence of anion impurities. Increasing SO_4^{2-} , Cl^- , or $\text{Cr}_2\text{O}_7^{2-}$ in solution raised the Tafel slope. The Ce(III)/Ce(IV) equilibrium potential decreased with the increase of SO_4^{2-} or Cl^- but was hardly influenced by $\text{Cr}_2\text{O}_7^{2-}$ addition. These observations from individual anion species together well explained the anions' co-effect (kinetic hindrance) on the Ce(III) oxidation in HNO_3 , revealing that these anions are unfavorable for the electrooxidation of Ce(III) in the spent Cr-etch solutions.

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1. Introduction

Ce(IV) species inherently are strong oxidizing agents. The addition of Ce(IV) into spent high-burn-up uranium fuels favors the dissolution of plutonium oxides and the removal of ruthenium; therefore, Ce(IV) can be used as a decontaminator in dissolution cells and connected pipes contaminated by radioactive nuclear species [1]. In addition, the Ce(III)/Ce(IV) redox system has attracted the attention in electroorganic synthesis for indirect oxidation of aromatic and alkyl aromatic compounds [2–3]. The Ce(III)/Ce(IV) redox couple is also attractive for developing environmental friendly redox flow batteries because of the couple's highly positive redox potential generating high cell voltage and large energy storage capacity for the batteries [4]. Nowadays, the importance of cerium in catalysis is rapidly growing with new applications in different fields [5]. It has been proposed about the potential uses of CeO_2 in the elimination

of soot from diesel engine exhaust, for the removal of organics from wastewaters, and as an additive for combustion processes [5]. Cerium ammonium nitrate [$\text{Ce}(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$] (CAN) dissolved in HNO_3 has recently been used as an etching solution for the semiconductor manufacturing processes and color filter industry. For example, the Ce(IV) from HNO_3 -dissolved CAN may oxidize Ru in chemical mechanical polishing processes [6]. In the color filter industry, the black matrix mainly made by complex chromium materials (Cr/CrO) is commonly used to enhance the color contrast, and the CAN (dissolved in HNO_3) is also the major component in the chromium etching (Cr-etch) solutions employed to transfer the pattern of black matrix [7]. In general, the concentration of CAN is close to 10–15% (~ 0.18 – 0.27 M) and the nitric acid is approximately 15% ($\sim 4 \text{ M}$) in the fresh Cr-etch solutions used in color filter manufacturing processes.

After use, Ce(IV) is reduced to Ce(III) in Cr-etch solutions and some impurities (e.g., SO_4^{2-} , Cl^- , and $\text{Cr}_2\text{O}_7^{2-}$) in the etching solutions possibly may lower the oxidation capacity of Ce(IV). The used Cr-etch solutions usually cause incomplete etching (residual black spots on etched surface) and affect the quality of color filter. As a result, these solutions (pH < 1 with

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high concentrations of HNO₃ and Ce(IV)) cannot be used further and become corrosive hazardous wastes that need to be treated. However, it is expensive to treat such spent Cr-etch solutions, and these solutions treated by conventional chemical precipitation methods usually generate considerable amounts of Cr-containing sludge with liability. The color filter manufacturers and semiconductor industries also need to purchase high-priced raw Cr-etch products. Therefore, it is very attractive for workers to recover/regenerate the spent Cr-etch solutions.

The electrochemical behaviors of Ce(III)/Ce(IV) couple on a few electrodes in some acidic (i.e., nitric, sulfuric, perchloric, and methanesulfonic) solutions were reported in literature [1,8–12]. Electrochemical methods potentially may also be applied to regenerate the spent Cr-etch solutions by oxidizing Ce(III) to Ce(IV) but the anion impurities such as SO₄²⁻, Cl⁻, and Cr₂O₇²⁻ present in the spent Cr-etch solutions possibly may influence the regeneration process. It is common that the spent chromium etching solutions from color filter manufacturing processes have major anion impurities of approximately 0.08 M Cl⁻, 0.025 M SO₄²⁻, and 0.016 M Cr₂O₇²⁻ (in addition to original ~4.0 M NO₃⁻) in the solutions. However, little is known for the anions' effect on the electrooxidation of Ce(III) in nitric acid. Accordingly, cyclic and linear sweep voltammetric measurements were used in this study to explore the Ce(III) oxidation on a glassy carbon electrode in 4 M nitric acid solutions with/without the anion impurities. The results obtained are useful for the evaluation of designing electrochemical systems employed to regenerate the spent Cr-etch solutions.

2. Experimental

The Ce(III) solution (0.02 M) without anion addition was prepared by dissolving Ce(NO₃)₃·6H₂O (analytical reagent grade, Research Chemicals Ltd.) into HNO₃ (4.0 M) (analytical reagent grade, Scharlau Co.). For the Ce(III) solution with anion addition, highly pure NaCl (Showa) and K₂Cr₂O₇ (Merck), and Na₂SO₄ (Merck) were added as the sources of Cl⁻, Cr₂O₇²⁻, and SO₄²⁻ anions, respectively. All solutions were prepared using deionised water with resistivities >18 M Ω cm⁻¹. The solutions were de-aerated by bubbling with nitrogen before experiments while the N₂ de-aeration was continued above the solutions during the experiments. All the experiments were performed at room temperature (25 ± 2 °C) in a 120 cm³ cell shown in Fig. 1.

The electrochemical behaviors of the couple Ce(III)/Ce(IV) in the prepared solutions were investigated with cyclic voltammetry (CV) and linear sweep voltammetry (LSV). The potential scan ranges were 0.8–1.7 V (anodic, 1 mV/s) and -0.5 ↔ 1.9 V (starting/ending at -0.5 V, 100 mV/s) for the LSV and CV measurements, respectively. Since the main focus in this work was Ce(III) oxidation, for the CV measurements, only the data in the 0.8–1.9 V range associated with the Ce(III) oxidation were provided. The formal potential was determined by the average peak redox potentials ((*E*_{p,a} + *E*_{p,c})/2) of Ce(III)/Ce(IV) couple. A CHI 660B electrochemical work station connected with a personal computer was used to conduct the voltammetric measurements. The working electrode was a glassy carbon disk

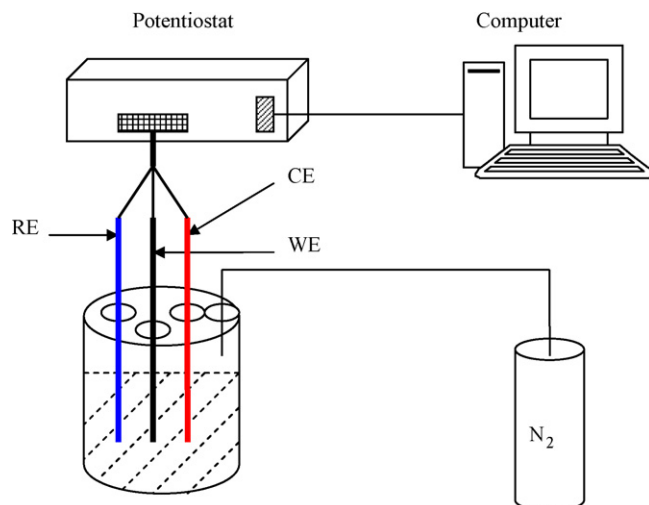


Fig. 1. The scheme of experimental device (CE: counter electrode, RE: reference electrode, and WE: working electrode).

(CH Instruments, Inc) electrode with an area of 0.07 cm² and the counter electrode was a platinum wire. An Ag/AgCl electrode (3 mol KCl dm⁻³, 0.207 V versus SHE (standard hydrogen electrode) at 25 °C) was used as the reference electrode. The potential reported in this work were all versus Ag/AgCl, unless particularly stated.

3. Results and discussion

3.1. Electrochemical behavior of Ce(III)/Ce(IV) in nitric acid

The cyclic voltammograms (100 mV/s) for 0.02 M Ce(III) in a 4.0 M nitric acid solution show that the oxidation of Ce(III) to Ce(IV) and its reverse reaction (reduction) peak at 1420 and 1220 mV, respectively (Fig. 2). The calculated formal potential of the Ce(III)/Ce(IV) couple was 1320 (= (1420 + 1220)/2) mV, close to a reported value (1380 mV) using a vitreous carbon electrode and a similar solution at room temperature [9]. The

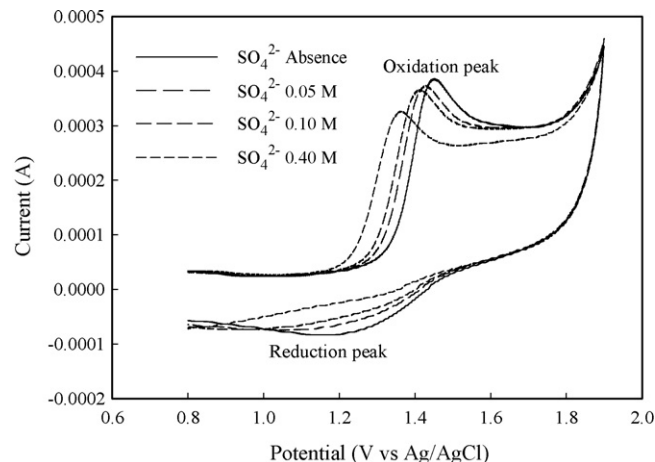


Fig. 2. Cyclic voltammograms (100 mV/s) for the 0.02 M Ce(III) in 4 M nitric acid solutions with/without the presence of SO₄²⁻.

ratio of cathodic peak current to anodic peak current (I_{pc}/I_{pa}) for the redox reaction of Ce(III)/Ce(IV) couple was about 0.21. This value is lower than that (0.45) reported by a study for 0.01 M Ce(III) in 1 M H_2SO_4 [13]. The discrepancy is mainly because of different electrolytes and electrodes used in experiments. Nevertheless, both the I_{pc}/I_{pa} values were far from unity, suggesting that there were kinetic or other complications in the electrode process [13]. It is possible that this electrochemical process was influenced by the oxidation of electrode carbon [4], and/or the complexation of Ce(III) with NO_3^- . The ~ 200 mV peak potential separation (ΔE_p , the potential difference between anodic and cathodic peak potentials) for the redox reaction indicates that the redox reaction of Ce(III)/Ce(IV) couple was an electrochemically quasi-reversible process [10].

3.2. Effect of SO_4^{2-} concentration on the oxidation/reduction of Ce(III)/Ce(IV)

The redox peak currents and potentials for the Ce(III)/Ce(IV) redox reaction decreased with increasing SO_4^{2-} concentration (Fig. 2). This trend was also observed for the couple's formal potential variation with SO_4^{2-} concentration. The formal potential gradually shifted to less positive values with increasing sulfate addition. This phenomenon, similar to that observed in a work [13], was attributed to the stronger complexation of sulfate than nitrate with Ce(III) [9] and thus the change in Ce(III) active species [13], resulting in a lower potential for the oxidation of Ce(III). Similarly, the increase of ΔE_p with the increase of SO_4^{2-} concentration from 0 to 0.4 M was also associated with more transformation from free cerium/cerous ions (or their nitrate complexes) into Ce(III)/Ce(IV)-sulfate complexes when the concentration of SO_4^{2-} was increased [13]. The SO_4^{2-} is easier to complex with Ce(IV) (generated from Ce(III) oxidation) than with Ce(III) [9], also leading to the more attenuation of Ce(IV) reduction with increasing SO_4^{2-} concentration. This attenuation of Ce(IV) reduction in voltammetry was also possible due to the formation of anionic Ce(IV) complexes with less affinity to electrode surface or the consumption of Ce(IV) in a follow-up chemical reaction (i.e., carbon oxidation on the glassy carbon electrode) [4].

In LSV tests (1 mV/s), the anodic current for Ce(III) oxidation increased at >1200 mV (Fig. 3(a)), similar to that found in the CV scans. A Tafel plot can be obtained by converting the current–potential data in a LSV scan into the $\log(\text{current})$ versus potential plot that corresponds to the Tafel equation below.

$$\eta = a + b \ln(I) \quad (1)$$

where η , a , b , and I are the overpotential (= applied potential – formal (equilibrium) potential), constant, Tafel slope, and current, respectively [14]. In order to correct the total overpotential for the mass-transport component, the Tafel equation can be replaced with the following mass transport-corrected Tafel equation.

$$\eta = -\frac{RT}{\alpha_a F} \ln I_0 - \frac{RT}{\alpha_a F} \ln \left(\frac{I_L - I}{I_L \times I} \right) \quad (2)$$

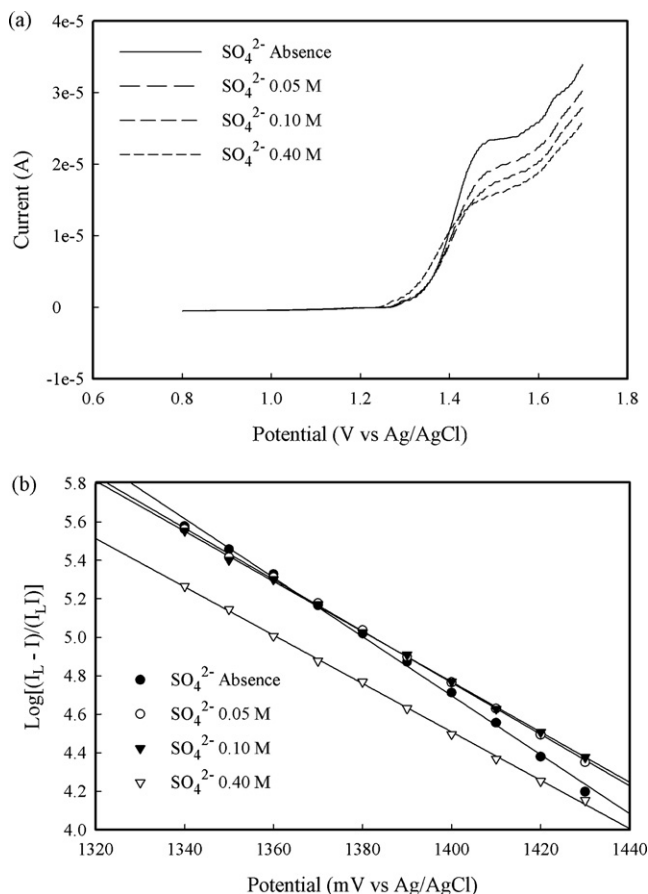


Fig. 3. Linear sweep voltammograms (1 mV/s) (a) and mass-transfer corrected Tafel Plots (b) for the 0.02 M Ce(III) in 4 M nitric acid solutions with/without the presence of SO_4^{2-} .

The symbols I_0 , I_L , and α_a represent the exchange current, mass-transport-controlled limiting current, and anodic transfer coefficient, respectively, while other symbols have their usual meaning [12]. For the Ce(III) oxidation reaction in 4 M HNO_3 (anions absence), the (mass transport-corrected) Tafel slope was ~ 65 mV decade $^{-1}$ (Fig. 3(b)). The anodic transfer coefficient (α_a) obtained was approximately 0.91 using the calculation of Tafel slope = $(2.3RT)/(\alpha_a nF)$, where R is the gas constant, T the absolute temperature, and n the number of electrons involved in the electrode reaction. Although the transfer coefficients of 0.3–0.7 are common for several electrochemical reactions, transfer coefficients beyond this 0.3–0.7 range may be found in electrochemical reactions, particularly if glassy carbon electrodes are used. For example, Denggerile et al. [15] obtained cathodic transfer coefficients (α_c) (= $1 - \alpha_a$) of 0.15–0.17, 0.14, and 0.072–0.083 for the electro-reduction of peroxyacetic acid at Au, Ag, and glassy carbon electrodes, respectively. The estimated apparent exchange current density for the Ce(III) oxidation was about 5×10^{-6} A cm $^{-2}$, implying that the Ce(III) oxidation in 4 M HNO_3 was not kinetically slow.

For the Ce(III) oxidation in 4 M HNO_3 in the presence of SO_4^{2-} , the variation of Tafel slopes and equilibrium potentials was slight at $SO_4^{2-} \leq 0.4$ M (Fig. 3(b)). In comparison to the case of SO_4^{2-} absence, the presence of 0.4 M SO_4^{2-} led to

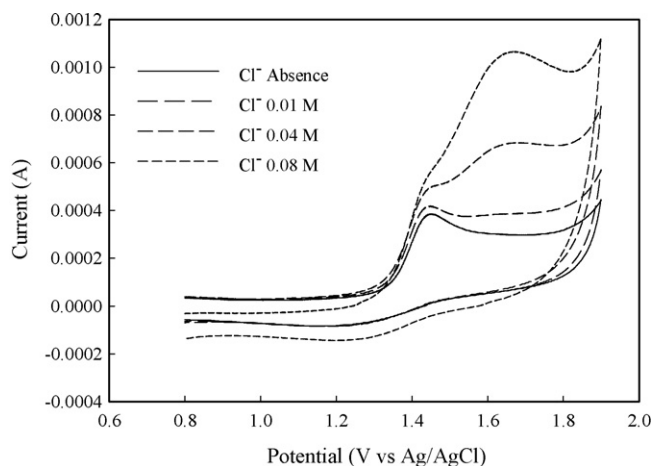


Fig. 4. Cyclic voltammograms (100 mV/s) for the 0.02 M Ce(III) in 4 M nitric acid solutions with/without the presence of Cl^- .

the increase of Tafel slope from approximately 65 to 80 mV decade^{-1} and the decrease of equilibrium potential from 1267 to 1239 mV. Therefore, the more the SO_4^{2-} , the slower is the redox kinetics. This finding also supports that more Ce(III)- SO_4^{2-} complexes possibly formed in the solution with higher SO_4^{2-} concentration are not electrochemically favored for the Ce(III) oxidation. Nevertheless, the exchange current densities obtained were in the 10^{-5} – 10^{-6} A cm^{-2} range.

3.3. Effect of Cl^- concentration on the oxidation/reduction of Ce(III)/Ce(IV)

When the SO_4^{2-} was replaced by Cl^- , both formal potential and peak potential separations were almost independent of Cl^- concentration in CV tests (Fig. 4). However, the anodic current at Ce(III) oxidation peak potential increased with increasing Cl^- concentration. This tendency can be explained by the partial overlap of the Cl^- oxidation peak (with a standard electrode potential of 1358 mV versus SHE) with the Ce(III) oxidation peak. At $\text{Cl}^- = 0.04$ M, the Cl^- oxidation peak apparently influenced the Ce(III) oxidation peak. This phenomenon was strengthened when the Cl^- concentration increased to 0.08 M. Since the required potentials for Cl^- and Ce(III) oxidation are closely overlapped, it is suggested to remove Cl^- before practical electro-regeneration operations if the glass carbon electrode is used.

Similarly, the anodic current increased with increasing Cl^- concentration in LSV scans (Fig. 5(a)). The increase of Cl^- also caused an increase in the Tafel slope for Ce(III) oxidation (Fig. 5(b)). Although the slope value hardly changed at low Cl^- concentration (≤ 0.04 M), the Tafel slope was up to 85 mV decade^{-1} at $\text{Cl}^- = 0.08$ M. This increase in Tafel slope may probably be attributed to the electrode-adsorbed Cl^- blocking the Ce(III) oxidation and/or the overlap of peaks for Ce(III) and Cl^- oxidation. Similar to the addition of SO_4^{2-} , the increasing addition of Cl^- ions caused an increasing negative shift in equilibrium potential for Ce(III) oxidation. This phenomenon can also be explained by the contribution of Cl^- oxidation to Ce(III) oxidation.

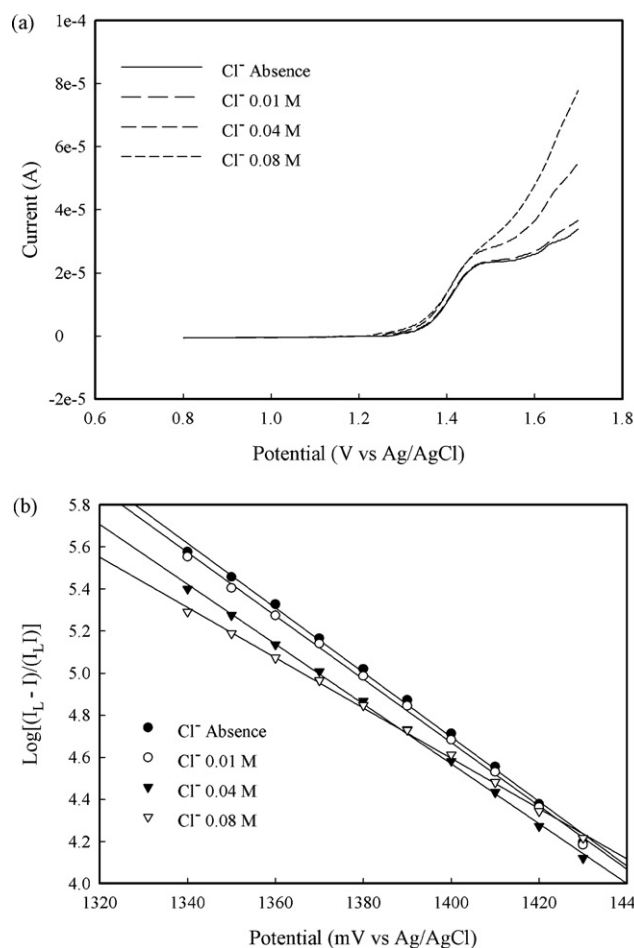


Fig. 5. Linear sweep voltammograms (1 mV/s) (a) and mass-transfer corrected Tafel Plots (b) for the 0.02 M Ce(III) in 4 M nitric acid solutions with/without the presence of Cl^- .

Pletcher and Valdes [9] indicated that the presence of 1 M NaClO_4 in either 1 or 5 M nitric acid did not change the CV results for cerous ion oxidation. In addition, Urbanski et al. [16] studied the extraction equilibriums of Ce(III) and La(III) from NaCl solutions with dodecylphenyl-methyl- β -diketone in *n*-heptane. They found that chloride did not participate in the constitution of extracted complexes to influence the extraction, implying that Cl^- was not favored to form complexes with Ce(III). It is also possible that Cl^- ions were not favored to form complexes with Ce(III) in this study; instead, they tended to absorb onto the electrode surface to hinder the Ce(III) electrooxidation.

3.4. Effect of $\text{Cr}_2\text{O}_7^{2-}$ concentration on the oxidation/reduction of Ce(III)/Ce(IV)

In general, the Cr(VI) speciation is chiefly dependent on the Cr(VI) concentration, pH, and redox potential of solution. Before the experiments, the Ce(III) in 4 M HNO_3 was colorless and the color of Ce(III) (0.02 M) + $\text{K}_2\text{Cr}_2\text{O}_7$ (0.005–0.016 M) in 4 M HNO_3 (with $\text{pH} < 1$) was orange implying that in the solution the dominant Cr(VI) anion species was $\text{Cr}_2\text{O}_7^{2-}$ [17], which was also supported by the hexavalent chromium specia-

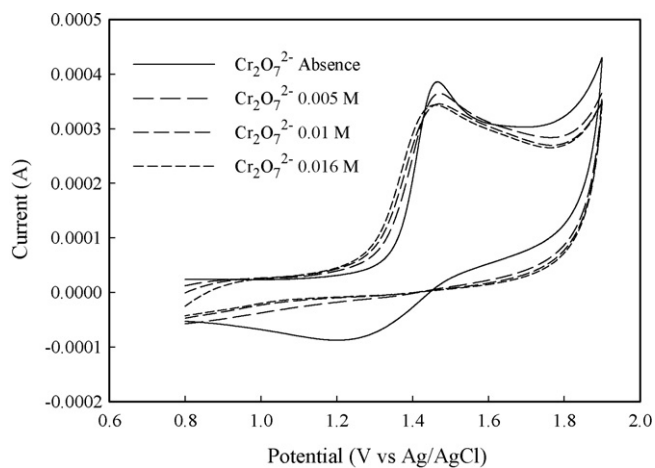


Fig. 6. Cyclic voltammograms (100 mV/s) for the 0.02 M Ce(III) in 4 M nitric acid solutions with/without the presence of $\text{Cr}_2\text{O}_7^{2-}$.

tion analyzed by Pourbaix [18]. Therefore, the influence of the Cr(VI) speciation partitioning between $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} on the Ce(III) electrooxidation is negligible.

Fig. 6 depicts that the CV peak current for Ce(III) oxidation slightly decreased with increasing $\text{Cr}_2\text{O}_7^{2-}$ concentration but the peak potential for Ce(III) oxidation was independent of $\text{Cr}_2\text{O}_7^{2-}$ concentration. This finding may be attributed to the adsorption of $\text{Cr}_2\text{O}_7^{2-}$ ions onto the electrode to block the Ce(III) oxidation. On the other hand, the Ce(IV) reduction peak attenuated with increasing $\text{Cr}_2\text{O}_7^{2-}$ concentration. At $\text{Cr}_2\text{O}_7^{2-} \geq 0.005$ M, the Ce(IV) reduction peak could not be evidently seen, probably resulted from the consumption of Ce(IV) by follow-up chemical reactions [4] or the passivation of electrode surface. The adsorption of dichromate ions on a copper mesh electrode was found to passivate the electrode surface to attenuate Cu^{2+} reduction in a 0.2 M KNO_3 (neutral pH) solution [19]. The inhibition of Cu^{2+} reduction by Cr(VI) was also observed at a planar Pt electrode in a 2.12 M chromic acid solution [20].

The LSV curves clearly show the gradual diminution of Ce(III) oxidation peak with increasing $\text{Cr}_2\text{O}_7^{2-}$ concentration in 4 M HNO_3 (Fig. 7(a)). Again, the increase of $\text{Cr}_2\text{O}_7^{2-}$ concentration resulted in the increase of Tafel slope (Fig. 7(b)). When the $\text{Cr}_2\text{O}_7^{2-}$ concentration increased from 0 to 0.016 M, the Tafel slope significantly increased from 65 to 100 mV decade⁻¹ (corresponding to the decrease of anodic transfer coefficient from 0.91 to 0.59) implying the increase of kinetic resistance for Ce(III) oxidation; nevertheless, the equilibrium potential hardly shifted, suggesting the Ce(III) species oxidized was almost not changed and thus indirectly reflecting the little formation of Ce(III)–Cr(IV) complexes.

3.5. Effect of multiple anions on the oxidation/reduction of Ce(III)/Ce(IV)

For practical purpose, the multi-anion condition (0.025 M SO_4^{2-} , 0.08 M Cl^- , and 0.016 M $\text{Cr}_2\text{O}_7^{2-}$) was tested and compared to the single anion addition cases for the anion effects on the Ce(III)/Ce(IV) redox reactions. The anodic CV current at

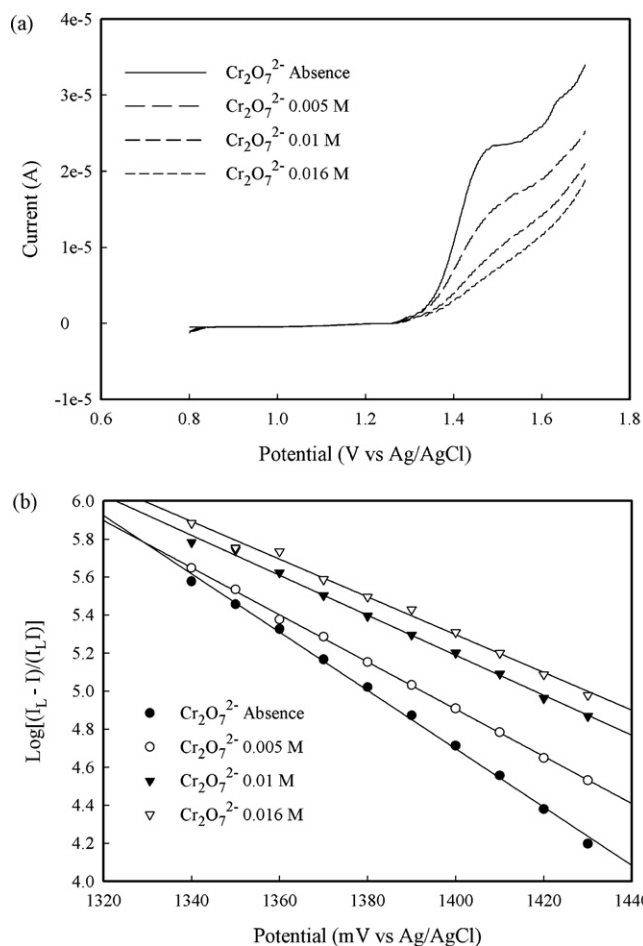


Fig. 7. Linear sweep voltammograms (1 mV/s) (a) and mass-transfer corrected Tafel Plots (b) for the 0.02 M Ce(III) in 4 M nitric acid solutions with/without the presence of $\text{Cr}_2\text{O}_7^{2-}$.

Ce(III) oxidation peak potential slightly decreased in the presence of multiple anions than in the absence of these anions (Fig. 8); however, this current increase for the multi-anion addition case was significantly lower when compared to that for the

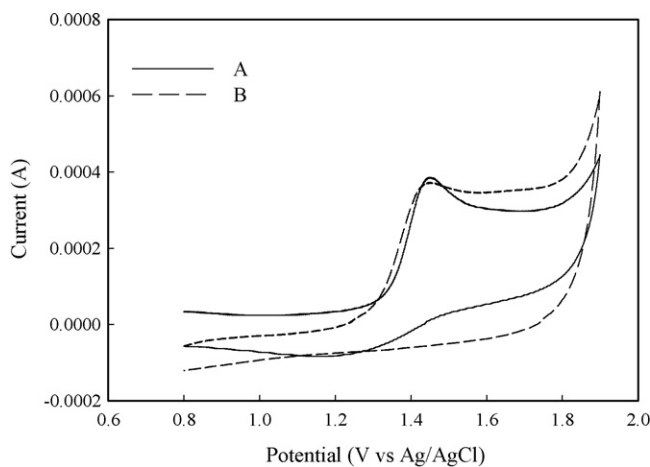


Fig. 8. Cyclic voltammograms (100 mV/s) for the 0.02 M Ce(III) in 4 M nitric acid (A) and the 0.02 M Ce(III) + 0.025 M Na_2SO_4 + 0.08 M NaCl + 0.016 M $\text{K}_2\text{Cr}_2\text{O}_7$ in 4 M nitric acid (B).

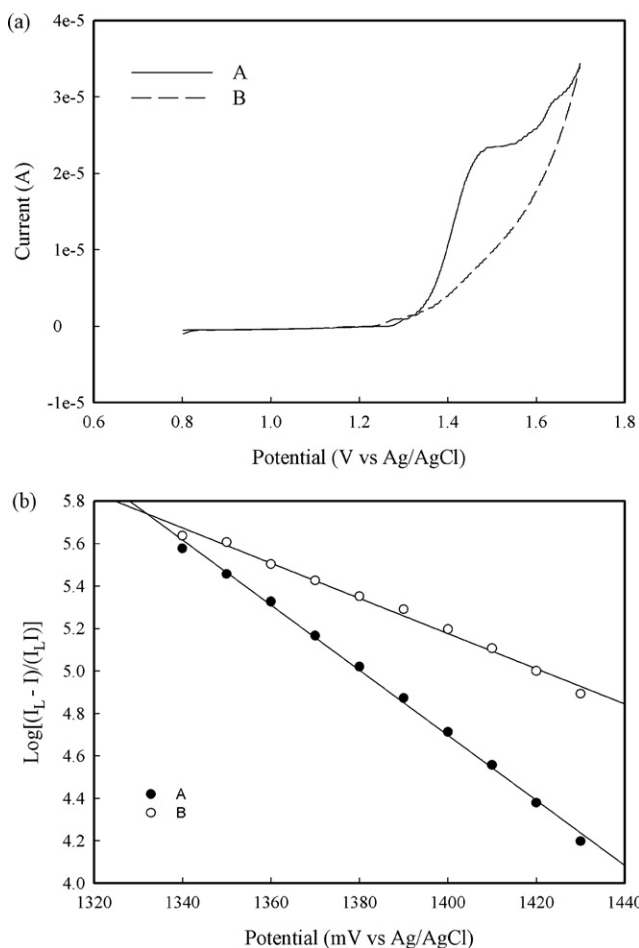


Fig. 9. Linear sweep voltammograms (1 mV/s) (a) and mass-transfer corrected Tafel Plots (b) for the 0.02 M Ce(III) in 4 M nitric acid (●) and the 0.02 M Ce(III) + 0.025 M Na₂SO₄ + 0.08 M NaCl + 0.016 M K₂Cr₂O₇ in 4 M nitric acid (○).

Cl⁻-only addition case, suggesting that the Cl⁻ oxidation was greatly inhibited. A possible explanation is that the Cr₂O₇²⁻ and SO₄²⁻ anions retarded the Cl⁻ adsorption onto the electrode surface, although the concentration of Cl⁻ was apparently higher than those of the Cr₂O₇²⁻ and SO₄²⁻. Also possibly due to the presence of Cr₂O₇²⁻, the peak for Ce(IV) reduction could not be clearly identified. On the other hand, no anodic peak corresponding to Cr(III) oxidation was observed, similar to that was reported for cyclic voltammetrically scanning Cr(VI) (1 mM) in a 0.1 M HCl solution using a glassy carbon electrode [21].

In LSV tests, the peak current for Ce(III) oxidation was also smaller in the presence of Cl⁻, SO₄²⁻, and Cr₂O₇²⁻ anions around the 1.4–1.6 V potential range (Fig. 9(a)). The inconsistency in observation between CV and LSV is mainly due to the large difference in scan rate for the two voltammetric scan cases and the combination effects of multi-anion on the Ce(III)/Ce(IV) redox reaction. According to Figs. 3(a), 5(a), and 7(a) for the single anion addition cases, the anodic LSV current decreased with increasing concentration of SO₄²⁻ or Cr₂O₇²⁻, but a reverse trend was found for the Cl⁻-only addition case. For the anodic LSV scan at the coexistence of these three anions, the current decrease from SO₄²⁻ and Cr₂O₇²⁻ was greater than the

current increase from Cl⁻ to result in a lower anodic current for Ce(III) oxidation at the coexistence than in the absence of the three anions. In addition, at the coexistence of Cl⁻, SO₄²⁻, and Cr₂O₇²⁻, the peak attenuation for Ce(III) oxidation was mainly due to Cr₂O₇²⁻ whereas the shift of equilibrium potential was chiefly because of SO₄²⁻ and Cl⁻; nevertheless, all the three anions contributed to the change of Tafel slope (Fig. 9(b)). Accordingly, unless the Cl⁻ and Cr₂O₇²⁻ are removed, a significant decrease in current efficiency is expected for the recovery of Ce(IV) from Ce(III) electrooxidation at 1.4–1.6 V versus Ag/AgCl using the glassy carbon electrode when all the three anions are co-present in the Cr-etch solutions.

4. Conclusions

In this work, significant anion effects on the Ce(III) electrooxidation process were observed. In CV tests, the presence of SO₄²⁻ (0.05–0.4 M) decreased the formal potential but increased the ΔE_p for Ce(III) oxidation, and lowered the peak current for Ce(IV) reduction. In contrast, both formal potential and ΔE_p for Ce(III) oxidation were independent of Cl⁻ concentration (0.01–0.08 M) but the peak for Ce(III) oxidation was partially overlapped by that for Cl⁻ oxidation (particularly at [Cl⁻] \geq 0.08 M). The peak current for Ce(III) oxidation slightly decreased but the Ce(IV) reduction peak significantly attenuated with increasing Cr₂O₇²⁻ concentration (0.005–0.016 M).

In LSV scans, the Tafel slope was ~ 65 mV decade⁻¹ in the absence of anion impurities. Increasing SO₄²⁻ or Cl⁻ in the 4 M HNO₃ led to the increase of Tafel slope and the decrease of equilibrium potential for Ce(III) oxidation. In the presence of Cr₂O₇²⁻ from 0 to 0.016 M in the acid solution, the Tafel slope significantly increased from 65 to 100 mV decade⁻¹ implying the increase of kinetic resistance for Ce(III) oxidation. The reduction of Ce(IV) also attenuated with increasing Cr₂O₇²⁻ concentration, probably resulted from the consumption of Ce(IV) by follow-up chemical reactions.

For the coexistence of 0.025 M SO₄²⁻, 0.08 M Cl⁻, and 0.16 M Cr₂O₇²⁻ in the 4 M HNO₃, the attenuation for Ce(III) oxidation was mainly attributed to Cr₂O₇²⁻ whereas the shift of equilibrium potential was chiefly because of SO₄²⁻ and Cl⁻; nevertheless, all the three anions contributed to the change of Tafel slope. Hence, it is unfavorable for the electrochemical oxidation of Ce(III) in the presence of these anions in the spent chromium etching solutions.

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