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Electrolytic oxidation of Ce(III) in nitric acid and sulfuric acid media using a flow type cell

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Abstract

The electrochemical oxidation behavior of Ce(III) in nitric acid and sulfuric acid media with various concentrations and compositions were investigated by cyclic voltammetry (CV) and potentiostatic electrolysis. In nitric acid media, the peak potential separation for the redox reactions of the Ce(III)/Ce(IV) couple shifted to base side with the increasing concentration of nitric acid from 1 to 6 M. The kinetics of the Ce(III)/Ce(IV) couple is rapid in high concentration nitric acid. The formal potential is independent of both proton and nitrate concentrations while the standard rate constant increases with added protons but is independent of nitrate concentration. Constant-potential electrolysis also shows that a high proton concentration is electrochemically favorable for the electron transfer of the Ce(III)/Ce(IV) couple and for a high Ce(IV) yield in nitric acid media. The current efficiency was ca. 75% for the oxidation process of Ce(III) at 298 K. A Ce(IV) yield of ca. 80% was achieved for the electrolysis of 100 mM Ce(III) in 6 M HNO_3 solution. In sulfuric acid media, the peak potential separation for the redox reactions of the Ce(III)/Ce(IV) couple shifted to noble side with rising concentration of sulfuric acid from 0.1 to 2 M and then shifted to base side with further increase in the concentration. A Ce(IV) yield of ca. 95% was achieved for the potentiostatic electrolysis of 100 mM Ce(III) in 3 M H_2SO_4 solution.

1. Introduction

When rare earth elements are separated and purified by the solvent extraction or ion exchange method, the ionic state of each elements is very important in separation yield and purification efficiency aspects. In our previous study, it was found that Ce(IV) had a much higher distribution coefficient than Ce(III) in concentrated nitric acid media and could be easily adsorbed onto AR-01 anion exchanger and separated from other rare earth elements [1]. In addition, it was reported that in spent high-burn-up uranium fuels, addition of oxidizing agent such as Ce(IV) favors not only the dissolution of plutonium oxide [2], but also the removal of ruthenium [3]. Ce(IV) can also be used as a decontaminator in the dissolution cell and connected pipes contaminated by radioactive nuclear species [4]. As the oxidizing agent, Ce(IV) is preferred because cerium is originally contained in fission products (FP) and the presence of Ce(IV) does not complicate the separation process of FP elements. To produce Ce(IV) in acidic media, electrochemical oxidation of Ce(III) has been employed by some researchers. Pletcher has reported the electrochemical behavior of Ce(III)/Ce(IV) couple in aqueous nitrate media [5], but no further study on electrolytic characteristics of Ce(III) has been reported. The electrochemistry of the Ce(III)/Ce(IV) couple in sulfuric acid solutions has been widely investigated [6–9]. However, the concentration of Ce(III) studied was fairly low, generally less than 50 mM. To examine the feasibility of electrolytic oxidation of Ce(III) with high concentration in acidic media, a systematic investigation onto the electrochemical oxidation behavior and electrolytic characteristics of Ce(III) and the influences of concentration, composition of the media and the temperature, were performed.

2. Experimental

The electrochemical behavior of the couple Ce(III)/Ce(IV), was investigated using cyclic voltammetry (CV) and constant-potential electrolysis techniques. The electrodes used for CV experiments include a glassy carbon disc with a diameter of 3 mm (area was ca. 0.07 cm^2) as the working electrode, a Pt disc as the counter electrode and a Ag/AgCl in 1 M KCl as the reference electrode. The solutions were de-aerated by bubbling with nitrogen before and during experiments.

The constant-potential electrolysis of the Ce(III) was conducted at 1500 mV (vs Ag/AgCl) with a plug-flow type cell as shown in Figure 1, in which a cylindrical porous glass (Vycor glass) (50 mm in length, 8 mm in inner diameter and 1 mm in thickness) was used as a separator. A bundle of carbon fibers of 20 μm in diameter together with a glassy carbon rod (2 mm in diameter) were inserted into the separator as the working electrode. A Pt wire (1.0 mm in diameter) was wound around the outer surface of the separator as the counter electrode. Ag/AgCl was used as the reference electrode. The apparent surface area for the working electrode was ca. 13 cm^2. The electrolysis cell was treated with 98% H_2SO_4 for 24 h prior to use. 50 ml of 100 mM Ce(III) in nitrate medium (or sulfuric acid) was used as the feed solution while the nitrate solution with the same composition but without cerium was contained in the counter-electrode compartment. The flow rate for the feed solution was 5 ml/min. The theoretical quantity of electric charge for complete oxidation of Ce(III) was calculated as 483 coulombs (0.134 Ah). The practical quantity of electric charge for the electrolysis was measured with a Coulomb meter (HZ-3000, Hokuto Denko Corp.). The ratio of the practical to theoretical electric-charge was calculated as electrolytic efficiency. The concentration of Ce(IV) was determined by redox potential titration using 10 mM Fe(II) in 1 M nitric acid as the reductant. Total concentration of cerium in the feed solutions was determined by ICP-spectroscopy.

3. Results and discussion

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

Figure 2 shows the cyclic voltammograms for 0.02 M Ce(III) in nitric acid solutions with various concentrations at a scan rate of 50 mV/s. The anodic peak at ca. 1550~1750 mV corresponds to the oxidation of Ce(III) to Ce(IV), and the corresponding reduction peak occurs at ca. 1300~1430 mV. It can be seen that the influence of nitric acid concentration mainly concerns two aspects 1) with increase in HNO_3 concentration, the peak currents corresponding to the oxidation of Ce(III) reduce due to the decrease in diffusion coefficients for the active species in the supporting electrolyte, which results from an increase in solution viscosity; 2) the peak potential separation (ΔE_p) for the redox reactions, defined as the potential difference between anodic and cathodic peak potentials, decreases from 431 to 124 mV with increase in HNO_3 concentration from 1 to 6 M, which means that the rate of the Ce(III)/Ce(IV) electron transfer increases markedly. The smallest peak potential separation obtained in 6 M HNO_3 supporting medium suggests that a high concentration of nitric acid is electrochemically favorable for the Ce(III)/Ce(IV) redox couple, which might partially be attributable to the introduction of carboxylic acid groups onto the electrode surface in concentrated nitric acid, resulting in a faster redox kinetics.

Figure 3 shows the cyclic voltammograms for 0.02 M Ce(III) in 6 M HNO_3 at various scan rates at 298 K. It can be seen that both the anodic and cathodic peak potentials changed slightly with the scan rates, and the peak potential separation look unchanged by the scan rate. A small peak potential separation is observed even at a fast scan rate, which means the rate of the Ce(III)/Ce(IV) electron transfer is fast in 6 M HNO_3. The formal potential ($E^{0'}$) of the Ce(III)/Ce(IV) couple in 6 M HNO_3 was estimated as 1490 mV from the cyclic voltammograms by taking the mean of the average of the anodic and cathodic peak potentials, E_{pa} and E_{pc}, i.e.,

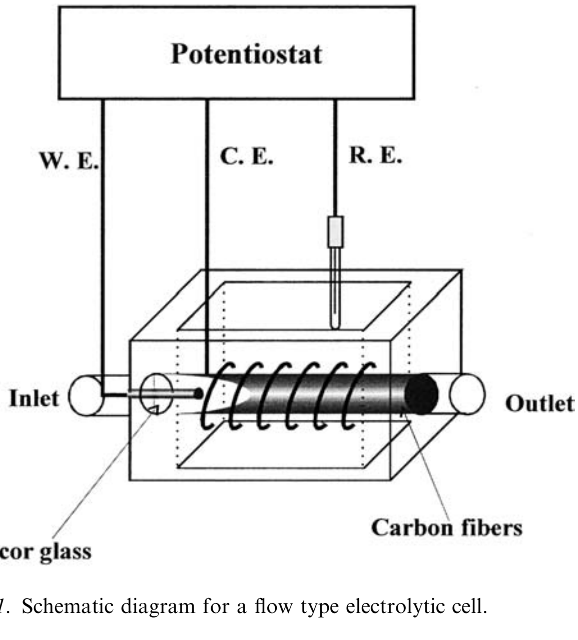

Fig. 1. Schematic diagram for a flow type electrolytic cell.

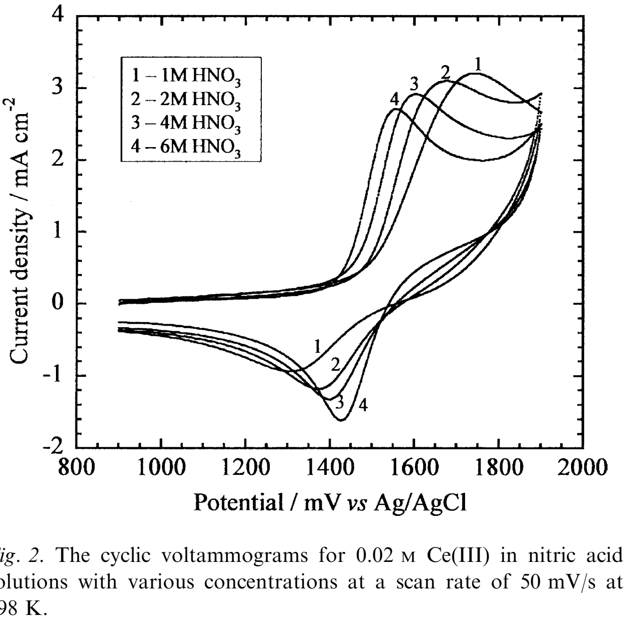

Fig. 2. The cyclic voltammograms for 0.02 M Ce(III) in nitric acid solutions with various concentrations at a scan rate of 50 mV/s at 298 K.

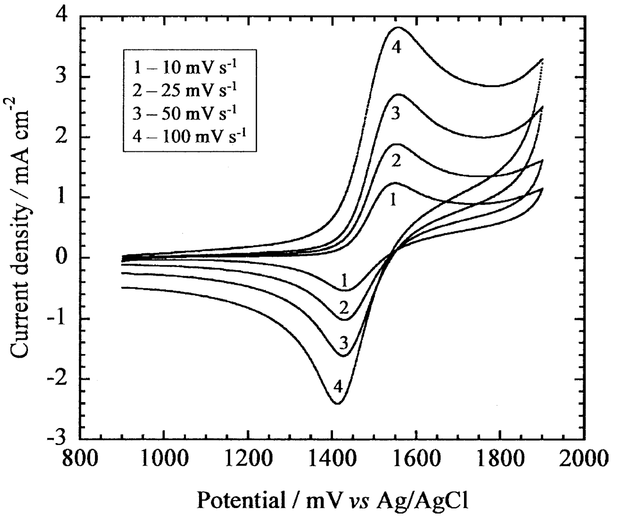

Fig. 3. The cyclic voltammograms for 0.02 M Ce(III) in 6 M HNO_3 at various scan rates at 298 K.

$$E^{0'} = \frac{\sum_{i=1}^{m}(E_{pai} + E_{pci})/2}{m} \qquad (1)$$

where m is the total number of scans (Figure 3).

From the above results, it is clear that high concentration of nitric acid is favorable for the electron transfer of the Ce(III)/Ce(IV) couple. However, the interpretation of data shown in Figure 3 is complicated because the concentration of both proton and nitrate ion is changing together. For this reason, experiments were carried out in solutions where only one is varying.

Figure 4 shows the cyclic voltammograms recorded at a scan rate of 50 mV/s for 0.02 M Ce(III) in nitrate solutions with 6 M NO_3^- and various proton concentrations.

It is evident that with the increasing proton concentration from 1 to 5 M the peak potential separation decreases substantially from 321 to 148 mV, which indicates that the increasing proton concentration promotes the electron transfer of the Ce(III)/Ce(IV) couple, probably because the activated complex can be involved in a protonation or deprotonation equilibrium [8]. It is also found that the formal potential for the Ce(III)/Ce(IV) couple is independent of proton concentration.

Some parameters for the Ce(III)/Ce(IV) couple in nitrate solutions, estimated from cyclic voltammograms recorded at 0.05 V/s, are summarized in Table 1, where diffusion coefficients D were estimated according to the following equation

$$i_p = 0.4463nFAC^*(nF/RT)^{1/2}v^{1/2}D^{1/2} \qquad (2)$$

where n, F, R and T have their usual significance. I_p, A, C^* and v are the peak current, surface area of the electrode, the concentration and scan rate, respectively.

The standard rate constant k^0 were estimated according to the Nicholson procedure as follows [10].

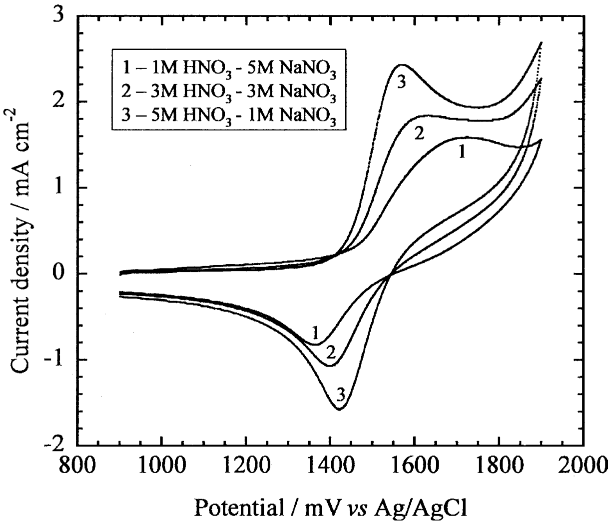

Fig. 4. The cyclic voltammograms recorded at a scan rate of 50 mV/s at 298 K for 0.02 M Ce(III) in nitrate solutions with 6 M NO_3^- and various proton concentrations.

Table 1. Parameters for the Ce(III)/Ce(IV) couple in nitrate solutions, estimated from cyclic voltammograms recorded at 0.05 V/s. Ce(III) concentration: 0.02 mol/dm^3

Solution conc./mol dm^{-3}		$E^{0'}$ /V vs Ag/AgCl	10^6D /cm^2 s^{-1}	10^2 k^0 /cm s^{-1}
[HNO_3]	[$NaNO_3$]			
1	5	1.52	5.5	0.4
3	3	1.51	6.2	1.1
5	1	1.50	6.8	2.3
6	0	1.49	6.9	2.6
1	0	1.52	8.8	0.2
1	1	1.53	8.7	0.3
1	3	1.53	7.3	0.3

$$\Psi = K^0/[D\pi v(nF/RT)]^{1/2} \qquad (3)$$

where Ψ stands for the degree of reversibility, and Ψ value can be estimated according to the peak potential separation [11]. It is found that the formal potential for the Ce(III)/Ce(IV) couple is also independent of nitrate ion concentration. The formal potential for the Ce(III)/Ce(IV) couple is independent of both nitrate ion and proton concentration which probably suggests that the complexation of both the predominant oxidized and reduced species in solution are similar, containing the same number of nitrate ligands, but in the case of Ce(IV), there are facile equilibria in involving the addition of nitrate which lead to $Ce(NO_3)_6^{2-}$ as follows [12].

$$Ce(NO_3)_3 - e = Ce(NO_3)_3^+ \qquad (4)$$

$$Ce(NO_3)_3^+ + 3NO_3^- = Ce(NO_3)_6^{2-} \qquad (5)$$

Table 2 shows some parameters obtained from the cyclic voltammograms for 20 mM Ce(III)–6 MHNO_3 at various temperatures. It is clear that the increase in the temperature from 298 to 333 K did not influence the formal potentials but it did increase as expected both the diffusion coefficient and the standard rate constant, which indicates that elevated temperatures are electrochemically favorable for the Ce(III)/Ce(IV) couple. The effect of temperature on the diffusion coefficient is displayed on an Arrhenius plot as shown in Figure 5. The value of the activation energy, E, is estimated from the slope ($-E/2.303$ R) as 16.3 kJ/mol. The electrode process of the Ce(III)/Ce(IV) couple in 6 M HNO_3 is mainly diffusion-controlled.

Figure 6 shows the cyclic voltammograms for 0.02 M Ce(III) in sulfuric acid solutions with various concentrations at a scan rate of 50 mV/s. It was found that the peak potential separation for the redox reactions of the Ce(III)/Ce(IV) couple increased with rising concentration of sulfuric acid from 0.1 to 2 M and then decreased with further increase in concentration. The changes in the peak potential separation might be associated with the changes in the existing forms of the predominantly active species, which changed from the free metallic ions of Ce(III)/Ce(IV) into the sulfate complex ions when the concentration of sulfuric acid increased. The smallest peak potential separation was observed for the Ce(III)/Ce(IV) couple in 0.1 M H_2SO_4 supporting electrolyte, which suggests that relatively low H_2SO_4 concentration is electrochemically favorable for the Ce(III)/Ce(IV) redox couple. However, from the electrolysis of Ce(III) in sulfuric acid media it was found that a marked hydrolysis of $Ce(SO_4)_2$ occurred when the concentration of H_2SO_4 was less than 0.5 M. On the other hand, it was found difficult to make a Ce(III) solution with a concentration greater than 100 mM in sulfuric acid media with concentration greater than 3 M. For these reasons, 0.5–3 M H_2SO_4 were selected as the supporting electrolytes for the electrolysis of Ce(III).

Table 2. Parameters for the Ce(III)/Ce(IV) couple in 6 M HNO_3 at various temperatures, estimated from cyclic voltammograms recorded at 0.05 V/s. Ce(III) concentration: 0.02 mol/dm^{-3}

Temperature /K	$E^{0'}$ /V vs Ag/AgCl	10^6 D /cm^2 s^{-1}	10^2 k^0 /cm s^{-1}
298	1.49	6.9	2.6
313	1.50	9.2	3.7
333	1.51	13.1	4.6

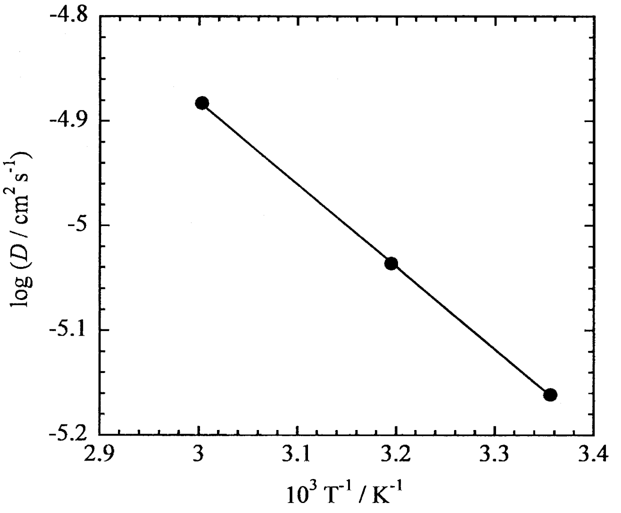

Fig. 5. Arrhenius plots of the diffusion coefficient of Ce(III).

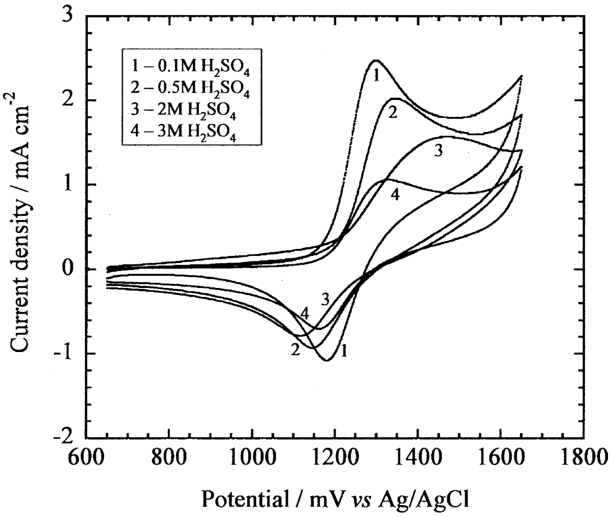

Fig. 6. The cyclic voltammograms for 0.02 M Ce(III) in sulfuric acid solutions with various concentrations at a scan rate of 50 mV/s at 298 K.

3.2. *Electrolytic characterization of the Ce(III)/Ce(IV) redox couple*

For further characterization of the Ce(III)/Ce(IV) redox couple in nitric acid and sulfuric acid media, constant-potential electrolyses at 1500 mV (vs Ag/AgCl) were conducted for 100 mM Ce(III).

Figure 7 shows the Ce(IV) yield against the electrolysis time for various nitrate solutions at 298 K. It is found that with increasing concentration of HNO_3 from 1 to 6 M the Ce(VI) yield increases greatly, i.e., from ca. 16 to 80% after 155 min of electrolysis. When the concentration of nitrate ion was set at 6 M while the proton concentration was varied as 1, 3, 5 and 6 M, respectively, a higher Ce(IV) yield was achieved at a higher proton concentration, indicating that protons accelerate the electron transfer of the Ce(III)/Ce(IV) couple in nitric acid media. In addition, it is found that the influence on the Ce(IV) yield is much smaller from the nitrate ion even though the concentration of NO_3^- changed greatly from 2 to 6 M.

A current efficiency of ca. 75% was obtained for the constant-potential electrolysis of 100 mM Ce(III)–6 M HNO_3. The relatively low current efficiencies might be attributed to the effects of side reactions such as the oxygen evolution, which may occur at a relatively positive electrode potential. In addition, the introduction of

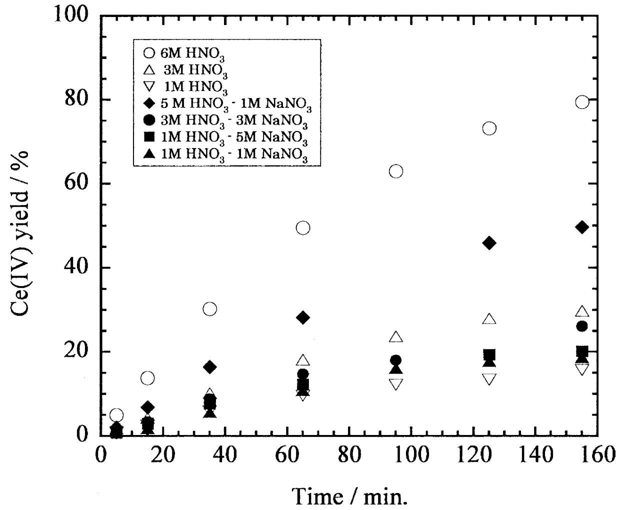

Fig. 7. The Ce(IV) yield shown against the electrolytic time for various nitrate solutions at 298 K.

carboxylic acid groups onto the electrode surface in concentrated nitric acid might facilitate the oxygen evolution.

Figure 8 shows the Ce(IV) yield against electrolysis time for various sulfuric acid media at 298 K. It is found that a highest Ce(IV) yield of ca. 95% was achieved in 3 M H_2SO_4, which was expected from the CV results.

In comparison with 3 M H_2SO_4, a lower Ce(IV) yield was achieved in nitric acid even in 6 M HNO_3. This is because sulfate forms stronger complexes with Ce(IV) than nitrate, resulting in a lower potential for the oxidation of Ce(III), which can be seen from the current–potential curves in Figure 9. Because the applied potential has a very important impact on the yield of the product for a potential-controlled electrolysis, influences of the applied potential on the yield of Ce(IV) and on the current efficiency are under investigation for various nitric acid and sulfuric acid media.

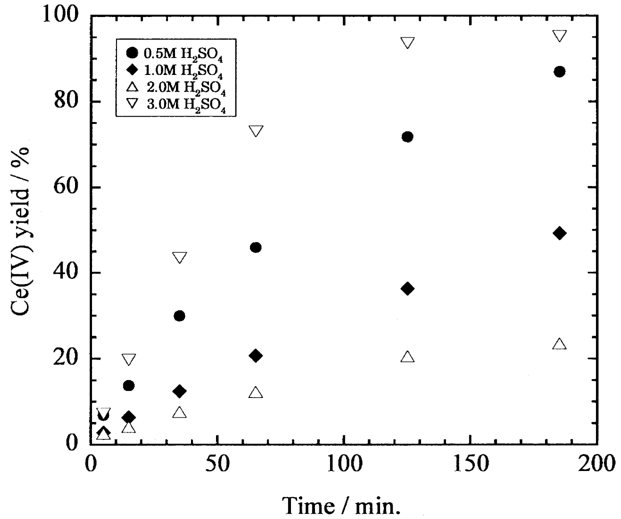

Fig. 8. The Ce(IV) yield shown against the electrolytic time for various sulfuric acid solutions at 298 K.

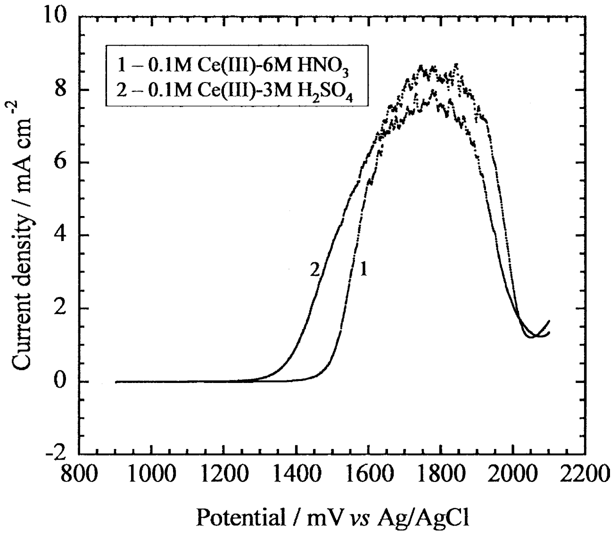

Fig. 9. The current–potential curves for 0.1 M Ce(III) in 6 M HNO_3 and in 3 M H_2SO_4 solutions at a scan rate of 1 mV/s at 298 K.

4. Conclusions

The electrochemical behavior of the Ce(III)/Ce(IV) couple in nitric acid and sulfuric acid media with various concentrations and compositions were investigated by cyclic voltommetry. In addition, the Ce(III)/Ce(IV) couple was further electrochemically characterized by the constant-potential electrolysis of 100 mM Ce(III) at 1500 mV (vs Ag/AgCl). The following conclusions can be drawn.

(i) The kinetics of the Ce(III)/Ce(IV) couple is rapid in high concentration nitric acid solutions.
(ii) High proton concentration promotes the electron transfer of the Ce(III)/Ce(IV) couple in nitric acid media.
(iii) The formal potential of the Ce(III)/Ce(IV) couple is independent of both nitrate ion and proton concentration.
(iv) The results from the constant-potential electrolysis of Ce(III) are highly consistent with those from CV measurements, i.e., a high proton concentration is electrochemically favorable for the electron transfer of the Ce(III)/Ce(IV) couple and for a high Ce(IV) yield in nitric acid media.
(v) A relatively high Ce(IV) yield in sulfuric acid is attributable to the relatively low oxidation potential of Ce(III).

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