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Nucleation and Growth of Anodic Electrodeposited Cerium Oxide Thin Film

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Cyclic voltammetry, chronoamperometry in conjunction with scanning electron microscopy and atomic force microscopy techniques have been performed to study the anodic electrodeposition behavior of ceria films onto 316L stainless steel substrate. Results show that the deposition process of ceria is controlled by diffusion under our experimental conditions. The dominated nucleation and growth mechanism for CeO₂ deposition transforms from two-dimensional (2D) to three-dimensional (3D) with increasing the deposition time, and 3D process starts prior to the completion of 2D layers. The poor conductivity of the preformed CeO₂ film causes the high deposition overpotential and therefore refines the grain size of CeO₂ particles.

Keywords: Anodic electrodeposition; Ceria thin films; Nucleation and growth mechanism

1. INTRODUCTION

Cerium dioxide, or ceria (CeO₂), possesses a cubic fluorite-type crystal structure, particularly versatile in accommodating oxygen deficiency, which results in n-type semiconducting properties [1]. Thanks to their chemical and physical characteristics, ceria thin films have emerged as a fascinating material due to many successful technological applications such as solid oxide fuel cells [2], polishing agents [3], catalysts for three-way catalysis of exhaust gas from automobiles [4], electrochromic [5], pharmacology [6], and coatings for corrosion protection of many metals and alloys [7-12].

Anodic polarization allows electrochemical oxidation of Ce^{3+} to soluble $Ce(OH)_2^{2+}$ (eq. (1)). The supersaturated $Ce(OH)_2^{2+}$ at the anode surface is deposited as solid CeO_2 (eq. (2)). [13]

$$Ce^{3+} + 2H_2O \rightarrow Ce(OH)_2^{2+} + 2H^+ + e^-$$

 $Ce(OH)_2^{2+} \rightarrow CeO_2 + 2H^+$

Electrodeposition is an alternative method for the formation of compound semiconductors on conducting substrates. It is an attractive route because of the cheap salt precursors, simple operation and the low cost of processing. [14] There have been several previous studies of the electrodeposition of ceria films on different substrate surfaces. [11, 15-23] Those studies mainly focused on either the generating pathway, [15-16] surface structures and characterizations [17-21] or the properties of ceria films [11, 22-23]. The information about the kinetics and mechanism of anodic nucleation of ceria is still sparse. However, when the film is electrodeposited, the nucleation and growth mechanism plays a crucial role on film structure and properties. [24]

(2)

In addition, many literatures have reported the early stages of metals or alloys using cathodic electrodeposition conditions. [25-29] Besides, Zhang and his collaborators [30] have studied the anodic film formation process of AZ91D magnesium alloy and suggested that the formation of AZ91D anodic film follows the mechanism of 3D nucleation with diffusion controlled growth and the nucleation type of anodic film changes from progressive to instantaneous with the increase of applied anodizing potential. Li et al. [31] have studied nucleation and growth of the cathodic electrochemical deposited cerium oxide films using in situ atomic force microscopy (AFM) for the first time. They proposed that the microscopic nuclei crystallized out from the intermediate gel mass, which serving as the growth centers of the new phase. Unfortunately, less information is available on the nucleation and growth mechanism of anodic electrodeposited CeO₂ films, which is helpful for obtaining good quality ceria thin films

The electrochemical nucleation and growth of metals is commonly investigated by electrochemical techniques, such as cyclic voltammetry (CV) and chronoamperometry (CA). They can both serve as the methods for deposition and be utilized as diagnostic tools for reaction mechanisms determination. On this basis, several models have been developed to interpret experimental measurements, based on certain assumptions involving the nucleation mode (instantaneous, progressive), the dimensional type of growth (2D, 3D), the geometry of growth centers, and the rate-determining step of the whole process. [28]

In this work, the electrodeposition behavior, especially the initial crystallization nucleation and growth mechanism of CeO_2 anodic electrodeposition on 316Lstainless steel were investigated in details using CV and CA techniques, and the morphological response to CeO_2 deposits was obtained by means of scanning electron microscopy (SEM) and AFM.

2. MATERIALS AND METHODS

A classical 3-electrode cell was used for all electrochemical experiments. A 316L stainless steel rod (SS, working area: 0.50 cm^2), was adopted as working electrode. Before each experiment, the working surface was polished to mirror using 2.5 µm diamond paste and rinsed with acetone and double-distilled water. The treated steel was further dried with nitrogen gas (N₂) stream and then

dipped into the anodic compartment for use. A saturated calomel electrode (SCE) connected through a salt bridge was used as reference, and a large platinum foil ($25 \times 25 \times 0.2$ mm) as counter electrode (cathodic compartment). The anodic and cathodic compartments were connected through a glass frit and the solutions used in these two compartments were always the same. All potentials were referred to SCE unless otherwise stated.

The electroplating bath is consisted of 0.05 M Ce(NO₃)₃·6H₂O (Sinopharm Chemical Reagent CO., Ltd. (SCRC), analytical reagent (AR), \geq 99.0%), 0.1 M CH₃COONH₄ (SCRC, AR) and doubledistilled water which was further purified with a Milli-Q purification system (Millipore, resistivity: 18.2 M Ω cm). All the measurements were performed in a quiescent solution. The solution temperature was controlled at 50 ± 0.1 °C by a thermostatically water bath.

CV and CA measurements were carried out using electrochemical workstation (CHI750 D). Cyclic voltammetry was performed in the -0.2 and 1.0 V potential range at different scan rates or in the baths containing different Ce^{3+} concentrations. The kinetic mechanism of CeO_2 deposition was studied under potentiostatic conditions by CA. The perturbation of the potential electrode started always at - 0.2 V (SCE) (open circuit potential) and the step was varied in the 0.40-0.65 V zone. After the CA experiments, the samples were washed with double-distilled water and dried by N₂ gas, then stored in a desiccator for further examination. Surface morphologies were observed using SEM (HitachiSU-8010) with an operating voltage of 5 kV. The AFM (Multimode 8) measurements were performed in air in the contact mode using standard-geometry silicon nitride probes (Digital Instruments) and all images were collected with a scan rate of 1 Hz.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry

The anodic electrodeposition behavior of ceria films onto 316L stainless steel (SS) substrate was first investigated using CV. Fig. 1 presents the cyclic voltammograms of 316L SS electrode in the deposition solutions with different Ce³⁺ concentration ($C_{Ce^{\pm}}$). There are two peaks (peak 1 and 2) in the anodic branch and only one peak (peak 3) in the cathodic branch. Peak 1 at around 0.2 V has been attributed to the anodic dissolution of 316L substrate for that, this peak dismissed when using glass carbon (GC) as the working electrode to conduct cyclic voltammetry at the same conditions, and almost no ceria oxides can be deposited on the substrate at this positive potential [32]. With the increase of $C_{Ce^{\pm}}$ from 0 M to 0.10 M, the current density of peak 2 increases, which definitely indicates this peak is caused by the oxidation of Ce³⁺ ions, and which is not under charge–transfer control [17]; whilst the potential position of peak 2 drifts negatively, which may also be ascribed to that the oxidation process is markedly influenced by the reactant concentration. Peak 3 locates at around 0.05 V except the one in the blank solution (without Ce³⁺), which can be attributed to the partial reduction of ceria film, since one would not expect the reaction Ce³⁺–CeO₂ to be fully reversible. [15]



Figure 1. The cyclic voltammetry curves of 316L SS in different concentrations of Ce^{3+} solution. (a) without Ce^{3+} , (b) 0.03 M, (c) 0.04 M, (d) 0.05 M, (e) 0.07 M, (f) 0.10 M. T= 50 °C, scan rate: 90 mV/s.

Fig. 2 shows the CV curves of different scan rate. The current density of peak 2 increases with increasing the scan rate, whilst, the peak potential of peak 2 shifts positively with increasing the logarithm of the sweep rate (Fig. 3), which is probably due to the non-reversibility of the process [33]. The value of the charge-transfer coefficient, α , was 0.28, which was estimated by applying the eq. (3) [33]:

$$\begin{array}{c} 0.9 \\ 0.8 \\ 0.7 \\ 0.6 \\ 0.5 \\ 0.6 \\ 0.5 \\ 0.6 \\ 0.5 \\ 0.6 \\ 0.5 \\ 0.4 \\ 0.2 \\ 0.1 \\ 0.2 \\ 0.1 \\ 0.2 \\ 0.1 \\ 0.2 \\ 0.2 \\ 0.0 \\ 0.2 \\ 0.0 \\ 0.2 \\ 0.0 \\ 0.2 \\ 0.0 \\ 0.2 \\ 0.0 \\ 0.2 \\ 0.0 \\ 0.2 \\ 0.0 \\ 0.2 \\ 0.0 \\ 0.2 \\ 0.0 \\ 0.2 \\ 0.0 \\ 0.2 \\ 0.0 \\ 0.2 \\ 0.0 \\ 0.2 \\ 0.0 \\ 0.2 \\ 0.0 \\ 0.2 \\ 0.0 \\ 0.2 \\ 0.4 \\ 0.6 \\ 0.8 \\ 1.0 \\ E/V \text{ s.SCE} \end{array}$$

$$\Delta E_{\rm p} / \Delta \log v = 2.3 RT / 2 \alpha nF \tag{3}$$

Figure 2. CVs of CeO₂ electrodeposition with different potential scan rate (in the unit of mV/s): (a) 20, (b) 30, (c) 40, (d) 70, (e) 90, (f) 110. T= 50 °C, $C_{Ce^{B+}}$ =0.05 M.



Figure 3. Variation of the anodic potentials of peak 2 with the logarithm of the sweep rate.

The diffusion of the electroactive species toward the surface of the working electrode is a critical factor. Nowadays, there exist different methodologies to determine the diffusion coefficient from the voltammetric data, however most of them only consider the peak currents and peak potentials, and do not take into account the rest information contained in the wave. In order to overcome this disadvantage, the convolution of the cyclic voltammograms has been carried out [34]. The key aspect of the convolutive potential sweep voltammetry [35], also referred to as semi-integral electroanalysis [36] is the convoluted (semi-integrated) current m(t), which could be used in a computer program to determine its values.

$$m(t) = \frac{1}{\pi^{1/2}} \int_0^t \frac{j(u)}{(t-u)^{1/2}} du$$
(4)

where j(u) is the current from the voltammogram. The limit value of the convoluted curve, m^* , results from the analysis of eq. (5), and it is independent of the reversibility, quasi-reversibility or irreversibility of the electrochemical system under study [36],

(5)

$$m^* = nFSC_0 D^{1/2}$$

where *n* is the number of exchanged electrons, *F* is the Faraday constant, C_0 is the bulk concentration of the electroactive species, *D* is the diffusion coefficient and *S* is the electrode surface area.

Fig. 4 shows an example of the cyclic voltammogram and its corresponding semi-integral curve. The convoluted curves obtained are very similar for the whole sweep rate range studied, however they do not remain identical from the direct to reverse scan, showing the non-reversibility of the deposition process [33]. The diffusion coefficient of the electroactive species can be computed from the boundary semi-integral values by means of eq. (5). The obtained results are listed in Table 1. In aqueous solutions, the average values of diffusion coefficients are around 10^{-5} cm² s⁻¹. [37] The lower values of diffusion coefficients in our study could suggest the electrodeposition process is mainly under diffusion-controlled.



Figure 4. CV (—) and their corresponding convoluted curves (---). T=50 °C, *C*_{Ce³}+=0.05 M, Scan rate is 110 mV/s.

Table 1. Diffusion coefficient calculated by different electrochemical techniques.

Technique	Cyclic voltammetry	Chronoamperometry
$D/(\times 10^8 \text{ cm}^2 \text{ s}^{-1})$	1.57	1.76

In addition, according to the prevailing mechanism [38], the logarithmic value of the rising current(*j*) near the peak position can be either proportional to the exponent of the reciprocal of overpotential $\left(-\frac{1}{|\eta|}\right)$ or the reciprocal of the squared overpotential $\left(-\frac{1}{|\eta|^2}\right)$, which stand for 2D (two-dimensional) and 3D (three-dimensional) nucleation and subsequent grain growth mechanisms, respectively. However, in our cases, the logarithmic value of the rising *i* near the apodic peak (Fig. 4)

respectively. However, in our cases, the logarithmic value of the rising *j* near the anodic peak (Fig. 4) seems to be approximatively proportional to both $1/\eta$ and $1/\eta^2$ (η is the overpotential) (Fig. 5), which may indicate that both 2D and 3D processes are concurrently involved in the deposition course of ceria film.



Figure 5. (a) The logarithmic value of the rising current (*j*) near the anodic peak vs $1/\eta$; (b) The logarithmic value of the rising current (*j*) near the anodic peak vs $1/\eta^2$ (η is the overpotential). Potential scan rate is 30 mV/s. T=50 °C, $C_{Ce^{B+}}=0.05$ M.

3.2. Chronoamperometry

In order to probe more details into the nucleation and growth mechanism, the ceria electrodeposition is further characterized by using chronoamperometry method. Fig. 6 shows the *j*-*t* experimental transients at 50 °C by setting the initial potential at -0.2 V (open circuit potential) and then stepping to a final potential comprised between 0.40 to 0.65 V i.e. the potential range where the oxidation of Ce^{3+} ions takes place. The general shape of the transients is independent of the final potential as would be expected for a nucleation and growth process [31, 39]. It can be clearly seen that, at initial time (within the first 0.02 s), there is a falling current transient that can be associated with the charging of the electrochemical double layer, which follows the Langmuir adsorption-desorption kinetics that can be expressed by the eq. (6) [40, 41].

$$j_{ad}(t) = k_0 \exp(-k_1 t)$$
 (6)

where $k_0 = k_1 Q_{ads}$ and Q_{ads} is the charge density due to the adsorption process. Then the value of current density increases slightly with increasing applied potential.



Figure 6. Current density-time curves obtained as a result of stepping the potential to different final values: (a) 0.4 V, (b) 0.5 V, (c)0.55 V, (d) 0.6 V, (e) 0.65 V. All initial potentials were -0.2 V. T= 50 °C, C_{Ce}^{s+}=0.05 M. Inset: Enlarged image.

We analyzed the linearization of the experimental current transients with time by means of the Cottrell equation $(j-t^{-0.5})$ (Fig. 7), which yielded approximatively linear relationships, indicating the electrodeposition process is mainly under diffusion-controlled [14]. This result is in accordance with that obtained by CV. Semi-integral electroanalysis could also be employed in the current density-time curves [36] and the calculated diffusion coefficient is also listed in Table 1, which is close to the result of convolutive potential sweep voltammetry.



Figure 7. The current density vs $t^{-1/2}$ according to the Cottrell equation.

The shape of the experimental transients implies that the very initial stage of the new phase formation may be appropriately illustrated by a two-dimensional (2D) nucleation and growth model. [40] The theoretical description of potentiostatic current transients bearing such characteristics has been developed by Armstrong and Harrison [42] for the case of two-dimensional nucleation controlled by diffusion. According to this model, the current density transients for instantaneous (j_{2Di}) and progressive (j_{2Dp}) nucleation could be described by eq. (7) and eq. (8).

$$j_{2Di}(t) = k_2 \exp(-k_3 t)$$
(7)

$$j_{2Dp}(t) = k_4 t \exp(-k_5 t^2)$$
(8)
where

$$k_2 = q_{mon} \pi S^2 D$$
(9)

$$k_3 = \pi S^2 D N_0$$
(10)

$$k_4 = q_{mon} \pi S^2 D A$$
(11)
and

$$k_5 = \pi S^2 D A/2$$
(12)

In these equations, q_{mon} is the charge density associated with the formation of the monolayer, D is the diffusion coefficient of the metal ion, S is a constant controlled by the potential, A is the nucleation rate and N_0 is the number density of active sites. However, any attempt to fit the curves of Fig. 6 to a simple 2D progressive and instantaneous nucleation and growth was failed. Thus, there may exists three-dimensional (3D) nucleation and growth mechanism, exactly as CV curves indicated (Fig. 2 and Fig. 5b). Such a mechanism seems to be quite likely because it is known that ceria is not very conducting [13, 43], so that the nucleation and growth processes of ceria tend to take place on the substrate firstly according to 2D mechanism, and after almost completing of one layer, 3D nucleation with diffusion controlled growth proceeds.

Up to date, the most widely employed theoretical model for electrochemical 3D nucleation is the one developed by Scharifker et al. [44]. This model derives explicit expressions for the current of progressive and instantaneous nucleation in the case of diffusion controlled growth of hemispherical (20)

clusters on a plane substrate [45]. According to this model, the current transient can be described, respectively for the instantaneous nucleation (j_{3Di}) and progressive nucleation (j_{3Dp}) by eq. (13) and eq. (14).

$$j_{3Di}(t) = k_6 t^{-1/2} [1 - \exp(-k_7 t)]$$
(13)

$$j_{3Dp}(t) = k_6 t^{-1/2} [1 - \exp(-k_8 t^2)]$$
(14)

$$k_6 = zFD^{1/2} c \pi^{-1/2}$$
(15)

$$k_7 = N \pi k D$$
(16)

$$k = (8 \pi c M / \rho)^{1/2}$$
(17)

$$k_8 = A N_{\infty} \pi k' D / 2$$
(18)

$$k' = \frac{4}{3} (8 \pi c M / \rho)^{1/2}$$
(19)

In the above equations, zF is the molar charge of electrodepositing species, c is the bulk concentration, D is the diffusion coefficient, M is the molar mass, N is the number of nuclei, N_{∞} and AN_{∞} are the total number of active sites for instantaneous nucleation and progressive nucleation respectively, k and k' are the numerical constants determined by the experimental conditions, and ρ is the density of the deposited material.

The entire process can be described in terms of the contribution of every step, namely:

$$j_{total}(t) = j_{ad}(t) + j_{2Di}(t) + j_{2Dp}(t) + j_{3Di}(t) + j_{3Dp}(t)$$

= $k_0 \exp(-k_1 t) + k_2 \exp(-k_3 t) + k_4 t \exp(-k_5 t^2) + k_6 t^{-1/2} [1 - \exp(-k_7 t)] + k_6 t^{-1/2} [1 - \exp(-k_8 t^2)]$

Fig. 8 shows a comparison between the experimental current density transients and the theoretical transients obtained by non-linear fitting of eq. (20). The parameters that gave the best fit are reported in Table 2. Results reveal that the experimental transient and the fitted transient matches very well with each other. In the applied potential range, strong overlapping of the processes is distinct. 2D process strongly overlaps with double layer charging in the beginning. Also, 3D process starts to grow prior to the completion of 2D layers [26]. In order to analyze the entire electrodeposition process in details, the current transients due to the 2D and 3D nucleation processes are separated from the total current transient, as shown in Fig. 9.





Figure 8. Experimental current transient recorded at different final potential and the fitted transient after non-linear fitting of Eq. (20). Contributions to the transient current from the double layer charging phenomenon and consecutive 2D and 3D growth process are shown separately. (a) 0.5 V, (b)0.55 V, (c) 0.6 V, (d) 0.65 V. Inset: Enlarged image.

Comparing the shape of the fitted 2D transients and Armstrong and Harrison's model curves [42], we can find that there exists both 2D instantaneous and progressive nucleation processes during the initial shorter time (t<0.2s), and then 2D progressive nucleation process disappears gradually (Fig. 8). Several seconds later (about t>2s), only 3D instantaneous nucleation process mainly exists, which can be proved by the parameters in Table2. The value of k_7 is much larger than k_8 , so that the 3D progressive nucleation process can be ignored.

E/V	0.5	0.55	0.6	0.65
$k_0/mA \cdot cm^{-2}$	9.98	14.37	17.54	20.06
k_1 / s^{-1}	15.47	16.73	16.33	19.65
$k_2/mA \cdot cm^{-2}(2Di)$	0.85	0.60	0.44	0.71
k ₃ / s ⁻¹ (2Di)	2.00	1.33	0.62	0.85
$k_4/mA \cdot cm^{-2} \cdot s^{-1}$ (2Dp)	3.27	4.62	4.80	6.38
k ₅ / s ⁻² (2Dp)	15.72	13.63	10.30	16.55
$k_{6}/mA \cdot cm^{-2} \cdot s^{1/2}$ (3D)	0.20	0.22	0.17	0.31
k ₇ / s ⁻¹ (3Di)	13343.78	1538.12	26824.82	1054.50
k ₈ / s ⁻² (3Dp)	5.84E-9	4.71E-14	6.63E-4	9.64E-5

Table 2. Parameter values of theoretical transients used to fit the experimental current transients presented in Fig. 8.



Figure 9. Individual contributions due to 2D nucleation (A) and 3D nucleation (B). Different final values: (a) 0.5 V, (b) 0.55 V, (c) 0.6 V, (d) 0.65 V.

3.3. Morphological study

The morphology images of the ceria deposits obtained at different potentials with constant deposition time of 2s are shown in Fig. 10. According to the SEM images, ceria particles present on the substrate surface after applying positive voltage, which suggests the three-dimensional growth mode, and both the size and amount of ceria particles increase with increasing the anodic potentials. When the deposition potential is high enough, these grains overlap with each other to cover fully the electrode surface.



(e)-0.2 V-0.6 V-2 s (e)-0.2 V-0.65 V-2 s

Figure 10. SEM image of the electrode surface at different final potentials: (a) blank, (b) 0.4 V, (c) 0.5 V, (d) 0.55 V, (e) 0.6 V, (f) 0.65 V. All initial potentials were -0.2 V. t = 2 s, T= 50 °C, $C_{Ce^{B+}}=0.05$ M.

Fig. 11 shows the morphology images of the ceria deposits obtained with different deposition time at 0.6 V. All the initial deposition process can be at least divided into two parts: In the first period of time (t<0.2s), many larger particles are formed, and they inhomogeneously/discretely distribute on the surface of 316L SS (Fig. 11a). The surface of 316L SS should contain many defects or imperfections such as plateau edges, kinks, vacancies and emergent screw dislocations of relatively high surface Gibbs free energy [46-47], therefore, the nucleation should first proceed on these points, which also results in the formation of new heterogeneous joints (between the already nucleated CeO₂ crystallites and 316L SS), which also possess relatively high surface Gibbs free energy. Because the conductivity of 316L SS is better than that of CeO₂, the further nucleation will mostly take place at the positions where exist both of the above formed joints and surface defects of 316L SS, which consequently results in the discrete distribution of many larger particles. Accordingly, the 2D instantaneous and progressive nucleation /growth mode dominated this period (Figs. 8-9 and Table 2). In the second period of time (t \geq 0.2 s) (Figs. 11b-d), the surface of 316L SS is almost covered with CeO₂ particles of poor conductivity, which increases the deposition overpotential and therefore results in the formation of small CeO₂ particles.



(c)-0.2 V-0.6 V-0.5 s (d)-0.2 V-0.6 V-1 s IIIII

Figure 11. SEM image of the electrode surface at different deposition time: (a) 0.1 s, (2) 0.2 s, (c) 0.5 s, (d) 1 s. Initial and final potentials were -0.2 V and 0.6 V respectively.

Accordingly, crystals of small and uniform size instead of the larger particles evenly distributed on the surface, and the amount of the smaller particles increases as time goes on, which proves that 3D process begins to dominate the deposition process. These smaller crystals of uniform size are as expected for 3D instantaneous nucleation. The results of SEM studies coincide exactly with the results from the fitted current transients (Figs. 8-9).

The morphologies of 316L substrate and the electrodeposited CeO₂ thin films were also characterized by AFM analysis. Fig. 12 presents 2D images of AFM of electrode surface before (a) and after (b-d) CeO₂ deposition at 0.65 V with different deposition time. The average roughness of electrode surface obtained by roughness analysis in AFM images was shown in Table 3. It can be seen from Fig. 12 and Table 3 that the deposited CeO₂ surface displayed a uniform and smooth topography with almost no cavity. Besides, with the prolongation of deposition time, the average roughness is found to first decrease due to the preferential nucleation and growth of CeO₂ at the surface defects of 316L and then increase due to the 3D process, which is in accordance with the results obtained from SEM (Fig. 11) studies, and also verifies the above elucidated transform of the nucleation and growth process from 2D to 3D (Figs. 8-9).





Figure 12. AFM image of the electrode surface at different deposition time: (a) blank, (2) 0.1 s, (c) 0.5 s, (d) 2 s. Initial and final potentials were -0.2 V and 0.65 V respectively.

Table 3. Average roughness obtained by roughness analysis of AFM images in Figure 12

Deposition time/s	Geometric area $/\mu m^2$	Average roughness/nm
0.0	25	1.92
0.1	25	1.50
0.5	25	1.33
2.0	25	1.65

4. CONCLUSIONS

The anodic electrodeposition of ceria films onto 316L stainless steel substrate has been studied by means of cyclic voltammetry, chronoamperometry, SEM and AFM technique. Under the experimental conditions, the deposition process of ceria is controlled by diffusion. The current-time transients can be theoretically well described with a transition from 2D to 3D nucleation. All the initial deposition process can be at least divided at least into two parts: In the first period of time (t<0.2s), the 2D instantaneous and progressive nucleation /growth mode plays a dominant role, and many larger flat particles are formed and discretely distribute on the surface of 316L SS. In the second stage (t \geq 0.2s), 3D instantaneous nucleation process begins to dominate the deposition process, the poor conductivity of the preformed CeO₂ film causes the high deposition overpotential, and therefore crystals of small and uniform size instead of the larger particles evenly distributed on the surface during this period.

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