Preparation of Cerium Oxide Films Using Pulse and Constant Electrodeposition Techniques

Sevil Cetinkaya[1,2*], Ruxandra Vidu[2] and Pieter Stroeve[2]
[1] Cumhuriyet University, Department of Chemical Engineering, 58140 Sivas, Turkey
[2] University of California Davis, Chemical Engineering and Materials Science, Davis, CA 95621, USA
*e-mail cetinkaya.sevil@gmail.com

Abstract: Ceria and ceria-based materials are becoming promising resources for a number of applications in microelectronics, electrochemical devices, ultraviolet blockers and surface treatment of different metals due to their corrosion resistance. These materials are also used for the development of electrochemical gas sensors in environmental applications and food industry since they have fast response, high sensitivity to threshold concentrations and low cost.

In this study, electrodeposition technique was used to prepare ceria film on nanostructured, gold-coated, polycarbonate track-etched membrane (PCTE) template. Both constant potential and pulse deposition techniques were used and the influence of deposition parameters on film surface characteristics was investigated. The structure and the electrochemical properties of the films were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis and energy dispersive spectrometry (EDS). A comprehensive electrochemical study was performed to understand the factors that could be controlled and optimized for a given set of surface properties. Surface properties of the ceria films were examined to study the impact of constant potential and pulsed electrodeposition techniques in creating ceria films.

Key words: Cerium oxide, electrodeposition, XRD, SEM, EDX

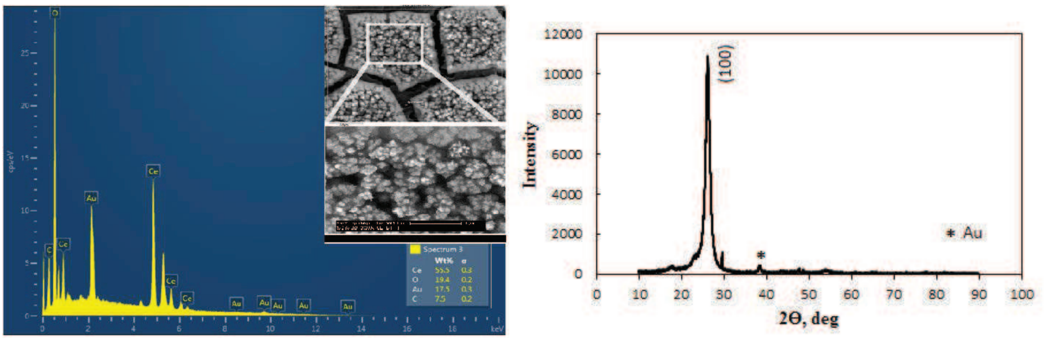

Figure: SEM images with the EDS pattern of the ceria films deposited at applied constant potential (-0.9V)

1. Introduction

Cerium is the most abundant element in the upper crust of the Earth among any other rare elements. Cerium oxide (ceria) and cerium based materials have been used in a number of applications such as catalysis, microelectronics, electrochemical devices, ultraviolet blockers and surface treatment of different metals and alloys due to their corrosion resistance to aggressive media [1-6]. These materials have also been used for the development of electrochemical gas sensors in clinical and environmental applications as well as in food industry since they have fast response and high sensitivity to threshold concentrations in addition to their low cost [7-9]. Additionally, cerium is an important material in solid oxide fuel cells (SOFCs), where both doped [10] and un-doped CeO_2 have been used [11].

Abundance of cerium combined with its excellent catalytic activity for a variety of reactions makes cerium the element of choice for the automotive industry, where it is used in the catalytic conversion of the exhaust system in automobiles. For example, ceria is being increasingly used to clean vehicle exhaust streams to reduce sulfur emissions [12, 13]. Catalytic activity of ceria is usually attributed to its high oxygen storage capacity (OSC), which is largely due to the multi-valence nature of cerium. Moreover, the shift between the cerium (III) (Ce^{3+}) to cerium (IV)(Ce^{4+}) leads to a high oxygen mobility in the ceria lattice and a strong catalytic potential. Cerium also has other uses in commercial catalysis, such as the production of styrene from ethyl-benzene and as cerium oxide in self-cleaning ovens.

Processing techniques such as sputtering, chemical vapor deposition [14], sol-gel processing [15] and electrodeposition [16] have been used for the formation of ceria films. Lately, electro-deposition of ceria has received considerable attention since the deposition can be carried out at low temperatures, does not require vacuum and can be produced at relatively low cost [17-21].

Anodic or cathodic electrodeposition is an attractive method since homogenous and chemically controllable nanostructured thin films can be obtained using inexpensive preparation [22-26]. Thin films of ceria have been electrodeposited onto Hastelloy substrates by the electrochemical oxidation of Ce(III) acetate complex. It was demonstrated that the deposition of ceria films by oxidation of Ce(III) stabilized with acetate ligands proceeds by one of two mechanisms, depending on the applied potential [19]. Liar et al. [5] studied the cathodic electrodeposition of ceria thin films. They confirmed the formation of cubic phase ceria by using X-ray diffraction and showed that the crystallinity could be improved after thermal treatment. Cathodic electrodeposition technique is well accepted as an inexpensive method to produce CeO_2 [27]. However, the aim of the electrochemical deposition of ceria is to obtain tailored composition cerium oxides in one-step electrodeposition and to eliminate the thermal treatment step. In this way, the substrate on which the ceria is deposited opens up to a multitude of materials, including flexible substrates.

Y. Kozu et al. [28] demonstrated the deposition of a composite thin film of Pt and CeO_2 on a glassy carbon (GC) electrode via single-step electro-chemical deposition technique. Although the actual reaction process of film formation is quite complicated, it is generally acknowledged that the oxidation of Ce^{+3} to Ce^{+4} state takes place in the presence of reactive species such as hydrogen peroxide, which is generated in situ during the following electrochemical oxygen reduction:

$$O_2 + 2H_2O + 2e- \rightarrow H_2O_2 + 2OH^- \qquad (1)$$

$$2Ce^{+3} + 2OH^- + H_2O_2 \rightarrow 2Ce(OH)_2^{2+} \qquad (2)$$

$$2Ce(OH)_2^{2+} + 4OH^- \rightarrow 2CeO_2 + 4H_2O \qquad (3)$$

Little attention has been paid to pulse electrodeposition (PED) as a technique to deposit porous cerium nanofilms. Pulsed electrodeposition is an effective method to control surface properties by varying pulse parameters, and to achieve a more homogeneous surface composition and morphology. In fact, thin film preparation by pulsed electrodeposition presents many advantages regarding the morphology and the composition of metal oxides and alloys [22, 29] but this method has not been applied to ceria yet. In this work, ceria film is deposited via cathodic deposition on nanostructured, gold-coated, polycarbonate track-etched membrane (PCTE) template by both constant potential and PED method. A comparison between these two methods is presented and the pulse parameters for porous ceria electrodeposition are investigated.

2. Materials and Methods

The electrolytic bath was consisted of 10 mM $Ce(NO_3)_3$, $6H_2O$ (Sigma Aldrich, 99.9%), 70 mM HNO_3 (Sigma Aldrich, 70%) and 1.5-3% vol H_2O_2 (Sigma Aldrich, 99.9%) in purified water (electrical resistivity 18.2 MΩ cm). Au was coated on the rough side of the PCTE membrane using a SEM sputtering device. The thin film deposition experiments have been performed on a nanostructured gold surface. A conventional three-electrode setup was used in electrolytic bath, where the Au-coated PCTE membrane was the working electrode. Cyclic voltammetry (CV) was performed to understand the electrochemical behavior of Au in the given solution. Cathodic electrodeposition was performed under potentiostatic and pulse conditions using a computer-controlled potentiostat (model EZstatPro). The reference electrode was Ag/AgCI electrode (3M NaCl). The counter electrode was a gold wire.

After electrodeposition, the samples were rinsed with ultra-pure water and dried in a nitrogen flow. Structural characterization was studied using a high-resolution scanning electron microscope (SEM) with energy-dispersive X-Ray spectroscopy (EDS) capability.

3. Results and Discussion

3.1. Sample Preparation: Electrochemical annealing

Before electrodeposition, the working electrode was cleaned in 50 mM H_2SO_4 according to the electrochemical annealing presented by Vidu et al. [23, 30] and the electrochemical behavior of the working electrode was investigated by cyclic voltammetry. The electrochemicla annealing involves 10-15 CV cycles between 0 and 1.5 V at a sweep rate of 50 mV/s followed by holding the sample at 0.9 V for about 10-15 min. During the electrochemical treatment, Au surface is cleaned and flattened as shown by the CV recorded before and after the annealing procedure (Figure 1).

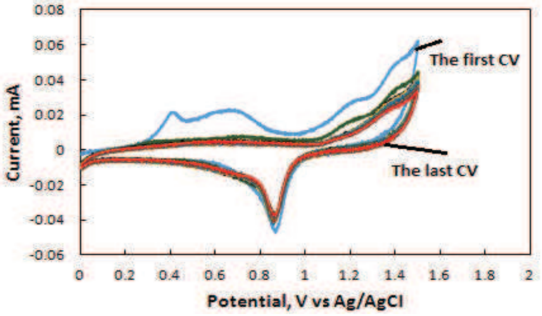

Figure 1: Cyclic voltammetry on Au in 50 mM H_2SO_4 solution before and after cleaning (sweep rate: 50 mV/s).

During the electrochemical annealing, Au surface atoms reorganize. Actually, while holding the potential at 0.9 V, the surface diffusion is high enough to reorganize the surface atoms and enlarge atomically flat terraces [31].

3.2. Constant Potential Deposition

Experimental runs using different amounts of H_2O_2 under two deposition potentials (-0.8V and -0.9V) were performed. Figure 2 presents the cyclic voltammetry responses of Au nanostructured surface in various solutions. All the CVs started at 0 V but had different vertex potentials. Figure 3 shows the current recorded during the deposition performed in certain deposition conditions.

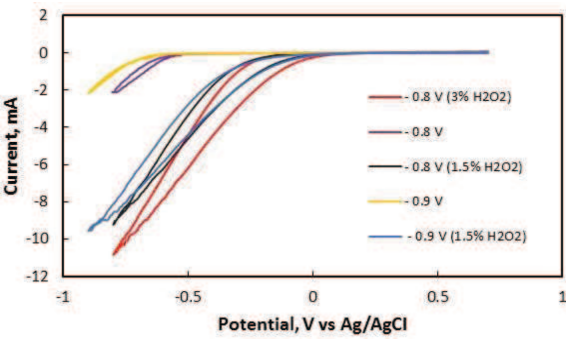

Figure 2: Cyclic voltammetry of Au film in 10 mM $Ce(NO_3)_3.6H_2O$ + 70 mM HNO_3+ xH_2O_2 (x=0, 1.5 and 3 % vol), at a sweep rate of 50 $mVs^{-1.}$

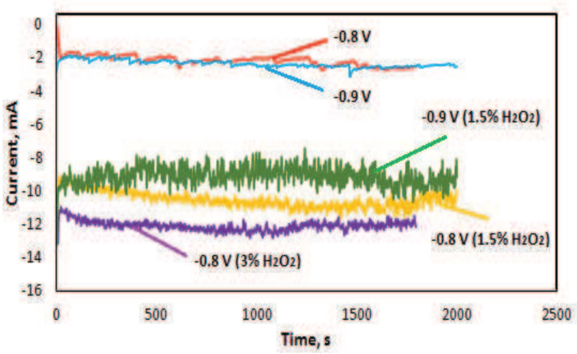

Figure 3: Variation of the current in time during the deposition of ceria in 10mM $Ce(NO_3)_3$, $6H_2O$ + 70mM HNO_3 for about 30 min at constant potential at room temperature.

Yousefi et al. [32] investigated the effect of H_2O_2 concentrations on the size and morphology of ceria nanoparticles. The addition of H_2O_2 results in a supplementary source for the generation of hydroxyl ions according to the following equation:

$$H_2O_2 + 2e \rightarrow 2OH^- \qquad (4)$$

Hydrogen peroxide prevents the formation of non-stoichiometric ceria film by oxidizing Ce(III) into Ce(IV) and enhances the adherence of the oxide films during electrodeposition [33].

Table 1 shows the variation of electrical charge associated with ceria deposition at various potentials and varying H_2O_2 amounts. Addition of more H_2O_2 to electrolyte (Table 1) increases the deposition current and the charge associated with ceria deposition at a given potential.

Table 1: Charge associated with deposition (C)

Charge, Q / **H_2O_2 (by volume)**	**Potential (V)**		
	-0.7	**-0.8**	**-0.9**
0	0.86	3.88	4.24
1.5	12.48	18.95	16.41
3	12.57	21.74	17.76

3.3. Pulse Potential Deposition

Figure 4 shows the current recorded during pulsed deposition conducted for 1h at two pulse conditions. The experiments presented in Figure 4 were performed at -0.9V / 0V and -0.7V / 0V with 10s on/1s off. During pulsed deposition, a larger current was observed for pulse deposition from -0.9V than from -0.7 V.

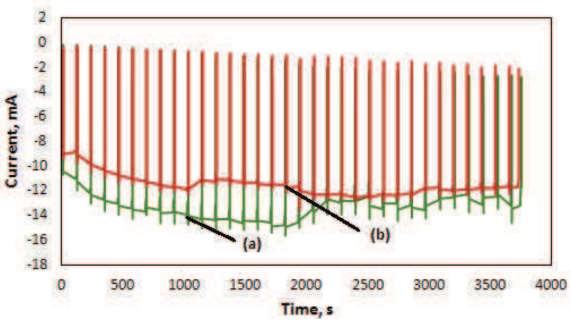

Figure 4: Variation of the current in time during the pulsed deposition of Ceria in 10mM $Ce(NO_3)_3.6H_2O$ + 70 mM HNO_3 + 1.5% H_2O_2 (by vol.) for 1 h at room temperature: a) -0.9 V/0 V and 10s on/1s off; b) -0.7V/0V and 10s on/1s off.

3.4. Characterization

Figures 5 and 6 show the SEM observations and the composition of the ceria film obtained under constant and pulse conditions, respectively. The film obtained under content potential deposition (Figure 5) has many cracks with a morphology that appears to be very porous while gold film on PCTE can be clearly seen in between the cracks. The edges of these formations appear to be foggy due to the oxide detachment from the gold substrate.

Figure 6 shows the morphology and the composition of the ceria film obtained under pulse conditions. The film is uniform with no cracks. Small, uniform size, islands are visible with no oxide layer or very thin oxide layer in between them. The ratio of O:Ce is about 3, which suggest the formation of a high hydrated oxide, CeO_3xH_2O, which can form in the presence of hydrogen peroxide.

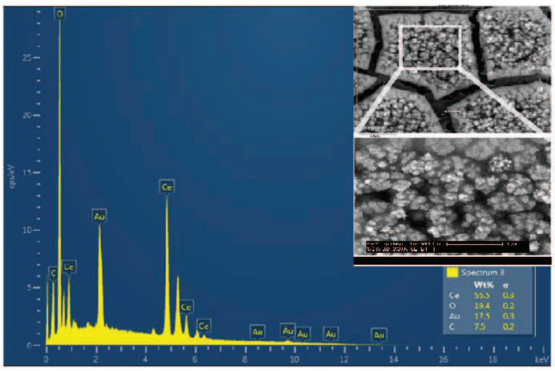

Figure 5: SEM morphology with EDS spectra of the ceria films deposited at -0.9V for 1h.

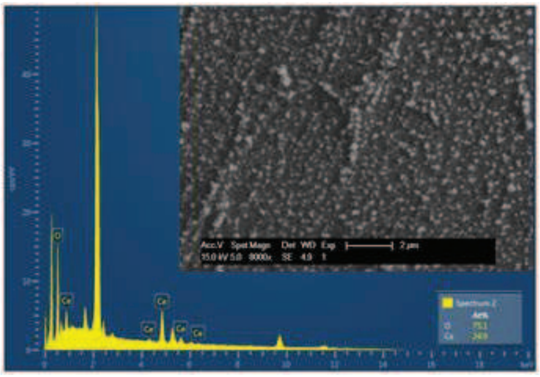

Figure 6: SEM morphology and EDS spectra of the ceria films deposited under pulse conditions (-0.8V/0V, 10s on/1s off) for 1 h.

To study the formation of ceria film, X-ray diffraction was used to analyze the films deposited in various conditions. XRD patterns in Figure 7 show that Ce_2O_3 was preponderantly obtained.

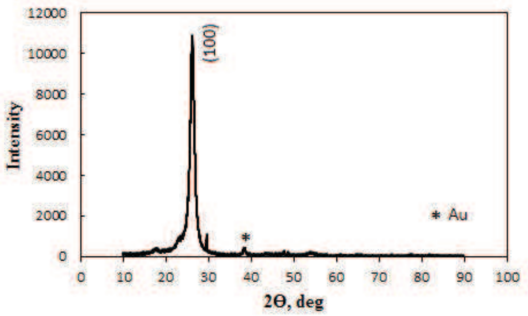

Figure 7: XRD pattern of ceria electrodeposited film (Ce_2O_3).

4. Conclusion

Ceria films were prepared by electrochemical catodic deposition in the presence of hydrogen peroxide. Both constant potential and pulse deposition techniques were applied. The deposition potentials and the amount of H_2O_2 in the solution were varied to investigate the ceria formation and morphology of ceria film under various deposition conditions. It was observed that both techniques were effective in forming ceria film by electrodeposition at room temperature. According to SEM, EDX and XRD, Ce_2O_3 film was preponderantly obtained under various experimental conditions. For sensor applications, gas sensitivity studies are currently being conducted to find the optimum experimental conditions correlated to the amount of ceria in the deposits.

5. Acknowledgment

This work was supported by the Scientific and Technological Research Council of Turkey with International Post-Doctoral Fellowship Program (2219) as a sabbatical fellowship to SC.

References

1. Balasubramanian, M., C.A. Melendres, and A.N. Mansour, Thin Solid Films, 347 (1999) 178.
2. Creus, J., et al., Surface & Coatings Technology, 200 (2006) 4636.
3. Fernandes, V., et al., Journal of the Electrochemical Society, 156 (2009) E199-E204.
4. Zec, S., et al., Ceramics International, 35 (2009) 195-198.
5. Liar, V., et al., Electrochemica Acta, 56 (2010) 784.
6. Wu, L.-K., et al., Surface & Coatings Technology, 204 (2010) 3920.
7. Durrani, S.M.A., et al., Sensors, 12 (2012) 2598.
8. Njagi, J., C. Ispas, and S. Andreescu, Analytical Chemistry, 80 (2008) 7266.
9. Yagati, A.K., et al., Biosensors & Bioelectronics, 47 (2013) 385.
10. Uhm, S., Y. Yi, and J. Lee, Catalysis Letters, 138 (2010) 46.
11. Zivkovic, L.S., et al., Russian Journal of Physical Chemistry A, 85 (2011) 2358.
12. Lawrence, N.J., PhD Thesis. University of Nebraska-Lincoln, 2010.
13. Ahrens, T.J., Global Earth Physics: A Handbook of Physical Constants. American Geophysical Union: Washington, D.C., 1995.
14. Toro, R.G., et al., Journal of Physical Chemistry B, 108 (2004) 16357.
15. Avellaneda, C.O. and A. Pawlicka, Thin Solid Films, 335 (1998) 245.
16. Bocchetta, P., M. Santamaria, and F. Di Quarto, Journal of the Electrochemical Society, 159 (2012) E108.
17. Balasubramanian, M., C.A. Melendres, and A.N. Mansour, Journal of the Electrochemical Society, 146 (1999) 607.

18. Golden, T.D. and A.Q. Wang, Journal of the Electrochemical Society, 150 (2003) C621-C624.

19. Kulp, E.A., et al., Solid State Ionics, 178 (2007) 749.

20. Phok, S. and R.N. Bhattacharya, Physica Status Solidi a-Applications and Materials Science, 203 (2006) 3734.

21. Santamaria, M., et al., Journal of the Electrochemical Society, 160 (2013) D212.

22. Quach, D.V., et al., Industrial & Engineering Chemistry Research, 49 (2010) 11385.

23. Vidu, R. and S. Hara, Scripta Materialia, 41 (1999) 617.

24. Vidu, R., J.-R. Ku, and P. Stroeve, Journal of Colloid and Interface Science, 300 (2006) 404.

25. Vidu, R., et al., Journal of Applied Electrochemistry, 42 (2012) 333.

26. Vidu, R., et al., Materials Science and Engineering B-Solid State Materials for Advanced Technology, 96 (2002) 199.

27. Wang, A.Q. and T.D. Golden, Journal of the Electrochemical Society, 150 (2003) C616.

28. Kozu, Y., S. Kawashima, and F. Kitamura, Journal of Solid State Electrochemistry, 17 (2013) 761.

29. de Tacconi, N.R., et al., Electrochemistry Communications, 5 (2003) 220.

30. Vidu, R. and S. Hara, Journal of Vacuum Science & Technology B, 17 (1999) 2423.

31. Vidu, R. and S. Hara, Surface Science, 452 (2000) 229.

32. Yousefi, T., A.N. Golikand, and M.H. Mashhadizadeh, Materials Science in Semiconductor Processing, 16 (2013) 1943.

33. Zhitomirsky, I. and A. Petric, Ceramics International, 27 (2001) 149.