Effect of heat treatment on the crystal structure and FTIR spectra of Sm doped cerium dioxide film

Xiaozhou LIU¹, a, Xiaozhou LIU², b, Letian XIA¹, c, Jie CHEN³, d and Xiaoyu WANG², e

¹GanNan Normal University Jiangxi, China 341000
²School of Chemical and Environmental Engineering, Shanghai Institute of Technology Shanghai, China 201418
³Regenia AB, Stockholm, Sweden 10691
⁴liuxiaozhou@yahoo.com, ⁵liuxiaozhen5291@163.com, ⁶xlt@sit.edu.cn,
⁷cj@yahoo.com, ⁸wxy@sit.edu.cn

Abstract. The Sm doped cerium dioxide films were prepared with cerium foils as raw materials by anodization in Sm(NO₃)₂-Na₂C₂O₄-NH₃·H₂O-H₂O-(CH₂OH)₂ electrolyte. The anodic Sm doped cerium oxide films were heat treated in 100°C ~ 400°C. The heat treated anodic Sm doped cerium oxide films were characterized with X-ray diffraction (XRD) and Fourier transform infrared (FTIR) techniques respectively. The heat treated anodic Sm doped cerium oxide film at 100°C is the semi crystalline film. As heat treatment temperatures being in 200°C ~ 400°C, the heat treated anodic Sm doped cerium oxide films have a structure of cubic fluorite respectively. The doping of Sm can be achieved well by anodization method and be recognized as replacement doping or caulking doping. The crystal structure of Sm doped cerium dioxide films become more complete with the increase of heat treatment temperature in 200 ~ 400 °C. The doping of Sm can improve the crystallinity of the cerium dioxide film. The presence of adsorbing water, ethylene glycol and CO₂ in the heat treated anodic Sm doped cerium oxide film at 100°C. The adsorbing ethylene glycols and water, CO₂ in the anodic Sm doped cerium oxide film are removed at 200°C and 300°C respectively.

1. Introduction
Because of doped cerium dioxide having high oxygen ion mobility and its multiple valence states, doped cerium dioxide has recently been attracting much attention in the oxidative catalysis and solid oxide fuel cell (SOFC) research communities ¹⁻⁹. The porous doped cerium dioxide films are potentially suitable for efficient catalytic treatment of reactants because such structures do not aggregate like particles which have diminished effective catalytic surface areas when used in bulk forms. They can also serve as media for separating reactants and products on different sides of the films such as in SOFC. The porous doped cerium dioxide film is prepared with cerium foils as raw materials, we may solve the existing problems, such as the controllability of thickness and density of film, defects by calcinations and high cost. The composition and crystal structure of the film have influence on the performance of the film.

In this paper, The Sm doped cerium dioxide films were prepared with cerium foils as raw materials by anodization in Sm(NO₃)₂-Na₂C₂O₄-NH₃·H₂O-H₂O-(CH₂OH)₂ electrolyte. The anodic Sm doped cerium oxide films were heat treated in 100 ~ 400°C. The heat treated anodic Sm doped cerium oxide films were characterized with X-ray diffraction (XRD) and Fourier transform infrared (FTIR) techniques respectively.
2. Experimental

2.1. Preparation of the Sm doped cerium dioxide films
The Sm doped cerium dioxide films were prepared by anodization in Sm(NO$_3$)$_3$·Na$_2$C$_2$O$_4$·NH$_3$·H$_2$O·H$_2$O·(CH$_2$OH)$_2$ electrolyte according to [10]. The electrolyte were 1.4 mmol/L Sm(NO$_3$)$_3$, 0.02 mol/L Na$_2$C$_2$O$_4$, 1 mol/L NH$_3$·H$_2$O aqueous ethylene glycol solution, ethylene glycol : H$_2$O = 10 : 1. The anodizing parameters: temperature 20°C, current density 0.5 mA/cm$^2$, time 10 h. The anodic Sm doped cerium oxide films were heat treated at 100°C, 200°C, 300°C, 350°C, 400°C, respectively for 2 h, and the Sm doped cerium dioxide film was got. The cerium dioxide film was prepared as contrast.

2.2. Testing instruments and methods
X-ray powder diffraction patterns of the heat treated anodic Sm doped cerium oxide films were acquired with a Rigaku D/max 2550 VB/PC X-ray diffractometer, using Cu Kα radiation, respectively. A continuous scan mode was used to collect 2θ data from 20 – 90° with a 0.02 sampling pitch and a 2° min$^{-1}$ scan rate. X-ray tube voltage and current were set at 40 kV and 30 mA, respectively.

Infrared absorption spectra of the heat treated anodic Sm doped cerium oxide films were determined by Avatar 360 FTIR infrared spectrophotometer by potassium bromide disc method respectively.

3. Results and discussion

3.1. XRD studies
The X-ray diffraction patterns of the anodic Sm doped cerium oxide films at different heat treating temperature are shown in Fig.1. The diffraction peaks 2θ of the films are shown in Table 1. As shown in Fig.1a and listed in Table 1, the heat treated anodic Sm doped cerium oxide film at 100°C has the
diffraction patterns at 28.54°, 33.08°, 47.54°, 56.32° respectively, the diffraction peaks correspond to cubic CeO$_2$(111), CeO$_2$(200), CeO$_2$(220), CeO$_2$(311), respectively, and the sample is the semi crystalline film. Comparing Fig.1b, Fig.1c, Fig.1d, Fig.1e, to Fig.1f, the diffraction peaks in the XRD spectra of the heat treated Sm doped cerium oxide films at 200°C, 300°C, 350°C, 400°C, respectively, can be recognized as the characteristic ones of CeO$_2$, which demonstrates that the samples have a structure of cubic fluorite respectively. Moreover, they give the diffraction peaks a small migration, which demonstrates that the doping of Sm can be achieved well by anodization method and be recognized as replacement doping or caulking doping. The ionic radius of Ce$^{4+}$ (92pm) and Sm$^{3+}$ (96.4pm) is about the same, the site replacement of Ce$^{4+}$ by Sm$^{3+}$. As shown in Fig.1b, Fig.1c, Fig.1d, Fig.1e, the intensity of diffraction peaks increase with the increase of heat treatment temperature in 200 ~ 400 °C, therefore, the crystal structure of Sm doped cerium dioxide films become more complete with the increase of heat treatment temperature in 200 ~ 400 °C. Comparing Fig.1e to Fig.1f, as heat treatment temperature being 400 °C, the intensity of diffraction peaks of Sm doped cerium dioxide film is stronger than that of the cerium dioxide film, which demonstrates that the doping of Sm can improve the crystallinity of the cerium dioxide film.

Table 1 Diffraction peaks 20 of films

| (hkl) | CeO$_2$(111) | CeO$_2$(200) | CeO$_2$(220) | CeO$_2$(311) | CeO$_2$(222) | CeO$_2$(400) | CeO$_2$(331) | CeO$_2$(420) | CeO$_2$(422) |
|-------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| 100°C | 28.54        | 33.08        | 47.54        | 56.32        |              |              |              |              |              |
| 200°C | 28.54        | 33.08        | 47.44        | 56.34        | 59.12        | 69.42        | 76.68        | 79.08        | 88.46        |
| 300°C | 28.56        | 33.10        | 47.44        | 56.30        | 59.12        | 69.42        | 76.70        | 79.08        | 88.42        |
| 350°C | 28.56        | 33.12        | 47.42        | 56.34        | 59.12        | 69.40        | 76.66        | 79.08        | 88.44        |
| 400°C | 28.52        | 33.10        | 47.44        | 56.36        | 59.12        | 69.42        | 76.66        | 79.06        | 88.42        |
| CeO$_2$ | 28.54        | 33.10        | 47.50        | 56.30        | 59.10        | 69.42        | 76.68        | 79.10        | 88.42        |

3.2. Infrared spectra

Fig.2 show FTIR spectra of the anodic Sm doped cerium oxide films at different heat treating temperature. According to Fig.2a, there are vO-H vibration peak at 3434.26 cm$^{-1}$, vCO$_2$ vibration peak at 2358.13 cm$^{-1}$, vO-H vibration peak at 1648.91 cm$^{-1}$, δCH$_2$ vibration peak at 1542.36 cm$^{-1}$, δO-H vibration peak at 1382.29 cm$^{-1}$, vC-O vibration peak at 1059.74 cm$^{-1}$, CeO$_2$ vibration peak at 400.00 cm$^{-1}$, demonstrating the presence of adsorbing water, ethylene glycol and CO$_2$ in the heat treated anodic Sm doped cerium oxide film at 100°C. According to Fig.2b, there are vO-H vibration peak at 3447.28 cm$^{-1}$, vCO$_2$ vibration peak at 2359.10 cm$^{-1}$, vO-H vibration peak at 1648.13 cm$^{-1}$, demonstrating the presence of adsorbing water and CO$_2$ in the heat treated anodic Sm doped cerium oxide film at 200°C. The adsorbing ethylene glycols in the anodic Sm doped cerium oxide film are removed at 200°C. According to Fig.2c and Fig.2d, there are CeO$_2$ vibration peaks at 610.42 ~ 400.00 cm$^{-1}$, demonstrating the heat treated anodic Sm doped cerium oxide film at 300°C and
400℃ respectively being Sm doped cerium dioxide film. The adsorbing water and CO₂ in the anodic Sm doped cerium oxide film are removed in 300℃ ~ 400℃. The Sm doped cerium dioxide film has strong absorption in the range of 1200 ~ 4000 cm⁻¹.

![FTIR spectra](image)

**Fig. 2** FTIR spectra of the anodic Sm doped cerium oxide films at different heat treating temperature

| Table 2 | The locations of infrared absorption spectra of the peaks (cm⁻¹) |
|---------|---------------------------------------------------------------|
| Heat treated film (100℃) | 3434.26 2358.13 1648.91 1542.36 1382.29 1059.7 400.00 |
| Heat treated film (200℃) | 3447.28 2359.10 1648.13 | 400.00 |
| Heat treated film (300℃) | 610.42 400.00 |
| Heat treated film (400℃) | 610.23 400.00 |

4. Conclusions
The heat treated anodic Sm doped cerium oxide film at 100℃ is the semi crystalline film. As heat treatment temperatures being in 200℃~ 400℃, the heat treated anodic Sm doped cerium oxide films have a structure of cubic fluorite respectively. The doping of Sm can be achieved well by anodization method and be recognized as replacement doping or caulking doping. The crystal structure of Sm doped cerium dioxide films become more complete with the increase of heat treatment temperature in 200 ~ 400 °C. The doping of Sm can improve the crystallinity of the cerium dioxide film. The presence of adsorbing water, ethylene glycol and CO₂ in the heat treated anodic Sm doped cerium oxide film at 100℃. The adsorbing ethylene glycols and water, CO₂ in the anodic Sm doped cerium oxide film are removed at 200℃ and 300℃ respectively.

**Acknowledgements**
This work was financially supported by the project supported by the National Natural Science Foundation of China (51372153, 51572176), Shanghai Municipal Education Commission (Plateau Discipline Construction Program, 0817), Leading Academic Discipline Project of Shanghai Municipal Education Commission (J51503).

**References**
[1] H.P. Dasari, K. Ahn, S.Y. Park, et al., Journal of Alloys and Compounds. 672 (2016) 397.
[2] M.L. Faro, S. Trocino, S.C. Zignani, et al., International Journal of Hydrogen Energy. 41 (2016) 5741.

[3] B. Timurkutlu, C. Timurkutlu, M.Y. Kaplan, Renewable and Sustainable Energy Reviews. 56 (2016) 1101.

[4] S.Y. Gomez, D. Hotza, Renewable and Sustainable Energy Reviews. 61 (2016) 155.

[5] W.L. Li, C.Y. Xiong, Q. Zhang, et al., Electrochimica Acta. 190 (2016) 531.

[6] S.Y. Gomez, D. Hotza, Renewable and Sustainable Energy Reviews. 61 (2016) 155.

[7] L.L. Guan, S. Le, X.D. Zhu, et al., Electrochimica Acta. 161 (2016) 129.

[8] T. Somekawa, Y. Matsuzaki, Y.Tachikawa, et al., Solid State Ionics. 282 (2015) 1.

[9] B. Matovic, M. Stojmenovic, J. Pantic, et al., Journal of Asian Ceramic Societies. 2 (2014) 117.

[10] X.Z. Liu, L.T. Xia, J. Chen, C.N. 201510503095.3.(2015).

[11] C.H. Wang, C. H. Lu, Mater Res Bull. 37 (2002) 783.