Preparation of Sm doped cerium dioxide film by anodization

Xiaozhen LIU\textsuperscript{1,*}, Junhua YANG\textsuperscript{1, b}, Xiaozhou LIU\textsuperscript{2, c}, Letian XIA\textsuperscript{1, d}, Jie CHEN\textsuperscript{3, e} and Ying ZHU\textsuperscript{1, f}

\textsuperscript{1}School of Chemical and Environmental Engineering, Shanghai Institute of Technology Shanghai, China 201418
\textsuperscript{2}GanNan Normal University Jiangxi, China 341000
\textsuperscript{3}Regenia AB, Stockholm, Sweden 10691
\textsuperscript{*}lixiaozhen5291@163.com, \textsuperscript{b}yjh@sit.edu.cn, \textsuperscript{c}liuxiaozhou@yahoo.com, \textsuperscript{d}xlh@sit.edu.cn, \textsuperscript{e}cj@yahoo.com, \textsuperscript{f}zy@sit.edu.cn

Abstract. The Sm doped cerium dioxide films were prepared with cerium foils as raw materials 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. The anodic Sm doped cerium oxide film was heat treated at 550°C. The Sm doped cerium dioxide films were characterized with X-ray diffraction (XRD), energy-dispersive analyses of X-ray (EDAX), Fourier transform infrared (FTIR) techniques and scanning electron microscopy (SEM), respectively. The anodic Sm doped cerium oxide film is semi crystalline film. The heat treated anodic Sm doped cerium oxide film at 550°C has a structure of cubic fluorite. The doping of Sm is replacement doping or caulking doping. The Sm doped cerium dioxide film is porous film. The water, ethylene glycol and CO$_2$ are adsorbed in the anodic Sm doped cerium oxide film. The adsorbing water, ethylene glycol and CO$_2$ in the anodic Sm doped cerium oxide film are removed at 550°C. The Sm doped cerium dioxide film has strong absorption in the range of 1200 – 4000cm$^{-1}$.

1. Introduction
Doped cerium dioxide has recently been attracting much attention in the oxidative catalysis and solid oxide fuel cell (SOFC) research communities, due to its high oxygen ion mobility and its multiple valence states \cite{1-3}. 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 common preparation methods of the porous doped cerium dioxide films are ball-milling and sintering methods. There are still some problems, such as controllability of thickness and density of film, defects by calcinations and high cost. If the porous doped cerium dioxide film is prepared with cerium foils as raw materials, we may solve the above problems.

In this paper, the Sm doped cerium dioxide films were prepared with cerium foils as raw materials 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, and the anodic Sm doped cerium oxide film was heat treated at 550°C. The Sm doped cerium dioxide films were characterized with X-ray diffraction (XRD), energy-dispersive analyses of X-ray (EDAX), Fourier transform infrared (FTIR) techniques and scanning electron microscopy (SEM), respectively.
2. Experimental

2.1. Preparation of the Sm doped cerium dioxide films
The Sm doped cerium dioxide films were prepared by anodization in $\text{Sm(NO}_3\text{)}_3$-$\text{Na}_2\text{C}_2\text{O}_4-\text{NH}_3\cdot\text{H}_2\text{O-}$ $\text{H}_2\text{O-(CH}_2\text{OH)}_2$ electrolyte according to [4]. High purity cerium foils ($99.99\%$ purity, $15\text{mm} \times 15\text{mm} \times 0.25\text{ mm}$) were used to grow anodic porous layers. Before anodization the cerium foils were degreased in absolute ethyl alcohol by using ultrasonic cleaner and annealed at $500^\circ\text{C}$ for $3\text{ h}$ to remove mechanical stresses and recrystallize of the cerium foils under a nitrogen atmosphere, and then polished with diamond spray polishing agent, followed in absolute ethyl alcohol by using ultrasonic cleaner. An electrochemical reactor was designed and built to carry out anodizing experiments, and got the anodic Sm doped cerium oxide film. The cerium foil and lead plate were the anode and the cathode respectively. The electrolyte were $1.4\text{ mmol/L}\text{ Sm(NO}_3\text{)}_3$, $0.02\text{ mol/L}\text{ Na}_2\text{C}_2\text{O}_4$, $1\text{ mol/L}\text{ NH}_3\cdot\text{H}_2\text{O}$ aqueous ethylene glycol solution, ethylene glycol : H$_2$O = 10 : 1. The anodizing parameters: temperature $20^\circ\text{C}$, current density $0.5\text{ mA/cm}^2$, time $10\text{ h}$. After anodizing, the anodized sample was washed thoroughly with distilled water, dried with an air jet, the anodized sample was heat treated at $550^\circ\text{C}$ for $2\text{ h}$, and the Sm doped cerium dioxide film was got.

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

The energy-dispersive analysis of X-ray of the heat treated anodic Sm doped cerium oxide film was acquired with S-3400N scanning electron microscopy.

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

The morphology of the Sm doped cerium dioxide films were examined by HITACHI S3400 scanning electron microscopy.

3. Results and discussion

3.1. XRD studies

Fig.1 XRD spectra of the anodic and the heat treated anodic Sm doped cerium oxide films
The X-ray diffraction patterns of the anodic and the heat treated anodic Sm doped cerium oxide films are shown in Fig.1. The diffraction peaks 20 of the films are shown in Table 1. As shown in Fig.1a and listed in Table 1, the anodic Sm doped cerium oxide film has the diffraction patterns at $28.52^\circ$, $32.94^\circ$, $47.56^\circ$, $56.34^\circ$ respectively, the diffraction peaks correspond to cubic CeO$_2$(111), CeO$_2$(200),
CeO$_2$(220), CeO$_2$(311), respectively. The anodic Sm doped cerium oxide film is semi crystalline film. Comparing Fig.1b to JCPDS Standard card (PDF#43-1002), the diffraction peaks in the XRD spectrum of the heat treated anodic Sm doped cerium oxide film at 550°C can be recognized as the characteristic ones of CeO$_2$, which demonstrates that the samples have a structure of cubic fluorite. Moreover, they give the diffraction peaks a small migration, which demonstrates that the doping can be achieved better by anodization method and be recognized as replacement doping or caulking doping. Comparing Fig.1b to Fig.1a, after the heat treatment of the anodic Sm doped cerium oxide film at 550°C, new diffraction peaks are observed at 59.10°, 69.40°, 76.70°, 79.06°, 88.48°, respectively, the diffraction peaks correspond to cubic CeO$_2$(222), CeO$_2$(400), CeO$_2$(331), CeO$_2$(420), CeO$_2$(422), respectively, and the crystal structure of the samples becomes complete.

| (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) |
|-------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| 25°C  | 28.52        | 32.94        | 47.56        | 56.34        |              |              |              |              |              |
| 550°C | 28.54        | 33.06        | 47.50        | 56.34        | 59.10        | 69.40        | 76.70        | 79.06        | 88.48        |

3.2. EDAX analysis

Fig.2 EDAX spectrum of the heat treated anodic Sm doped cerium oxide film at 550°C

Fig.2 shows the EDAX spectrum of the heat treated anodic Sm doped cerium oxide film at 550°C. The contents of Ce(at%), Sm(at%) and O(at%) are 31.67%, 1.09% and 67.24% respectively, and Ce(at%) + Sm (at%) : O(at%) =1.2. The heat treated anodic cerium oxide film at 550°C is the Sm doped cerium dioxide film. The result is consistent with the XRD analysis result.

3.3. Infrared spectra

Fig.3 FTIR spectra of the anodic and the heat treated anodic Sm doped cerium oxide films
Fig. 3 show FTIR spectra of the anodic and the heat treated anodic Sm doped cerium oxide films. According to Fig. 3a, there are νO-H vibration peak at 3423.17 cm⁻¹, νCO₂ vibration peak at 2360.54 cm⁻¹, νO-H vibration peak at 1632.03 cm⁻¹, δCH₂ vibration peak at 1544.28 cm⁻¹, δO-H vibration peak at 1383.73 cm⁻¹, νC-O vibration peak at 1059.34 cm⁻¹, CeO₂ vibration peak at 400.00 cm⁻¹, demonstrating the presence of adsorbing water, ethylene glycol and CO₂ in the anodic Sm doped cerium oxide film. According to Fig. 3b, there are CeO₂ vibration peaks at 600.00 ~ 400.00 cm⁻¹, demonstrating the heat treated anodic Sm doped cerium oxide film at 550°C being Sm doped cerium dioxide film. The adsorbing water, ethylene glycol and CO₂ in the anodic Sm doped cerium oxide film are removed at 550°C. The result is consistent with the XRD analyses and EDAX analyses result respectively. The Sm doped cerium dioxide film has strong absorption in the range of 1200 ~ 4000 cm⁻¹.

|                  | Anodic Sm doped cerium oxide film | Heat treated film (550°C) |
|------------------|----------------------------------|--------------------------|
| νO-H vibration peak | 3423.17 | 400.00 |
| νCO₂ vibration peak | 2360.54 |             |
| νO-H vibration peak | 1632.03 |             |
| δCH₂ vibration peak | 1544.28 |             |
| δO-H vibration peak | 1383.73 |             |
| νC-O vibration peak | 1059.34 |             |
| CeO₂ vibration peak | 400.00 |             |

3.4. SEM image

Fig. 4 shows SEM surface morphology of the Sm doped cerium dioxide film. It is seen in Fig. 4 that the Sm doped cerium dioxide film is the porous film.

![SEM image of Sm doped cerium dioxide film](image)

Fig. 4 SEM of the Sm doped cerium dioxide film (×3000)

4. Conclusions

The Sm doped cerium dioxide film is prepared by anodization in Sm(NO₃)₃-Na₂C₂O₄-NH₃-H₂O-H₂O-(CH₂OH)₂ electrolyte. The anodic Sm doped cerium oxide film is semi crystalline film. The heat treated anodic Sm doped cerium oxide film at 550°C has a structure of cubic fluorite. The doping of Sm is replacement doping or caulking doping. The Sm doped cerium dioxide film is porous film. The water, ethylene glycol and CO₂ are adsorbed in the anodic Sm doped cerium oxide film. The adsorbing water, ethylene glycol and CO₂ in the anodic Sm doped cerium oxide film are removed at 550°C. The Sm doped cerium dioxide film has strong absorption in the range of 1200 ~ 4000 cm⁻¹.

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