Research Article

Preparation of Cerium Dioxide Layers on Titanium by Electrodeposition with Organic Solution

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Layers of cerium dioxide nanoparticles were prepared on titanium by electrodeposition with organic solution. Three concentrations of cerium ions were used at 31.6 V. The organic solution was isobutanol and titanium foils were used as anodes and cathodes. Currents were monitored during the electrodeposition. Deposition times ranged from 0.5 to 8 h. Deposited layers were calcined at 700 K for 30 min. The morphology and composition of the deposited layers were examined by scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). As-prepared and calcined deposition layers were assayed to be cerium dioxide. The average crystallite size increased from 4 to 7 nm through calcination at 700 K. Sizes of calcined cerium oxide agglomerates were ranging from 73 to 146 nm for 30 min deposition and 209 to 262 nm for 8 h deposition. The electrodeposition efficiencies of 0.5 h deposition at three concentrations were measured to be highest.

1. Introduction

Targets of cerium dioxide with thicknesses in range of several mg/cm² were used in proton-induced nuclear reactions [1–3]. Cerium dioxide was deposited on aluminum. Targets of cerium dioxide with a thickness in range of mg/cm² deposited on titanium can be used to verify cross sections of production of $^{142}$Pr whose values were reported to disagree at proton energies in the vicinity of 12 MeV [1, 2]. Titanium has been used to precisely monitor the proton energy up to 30–40 MeV using the $^{nat}$-Ti(p,xn)$^{148}$V nuclear reaction [4–6].

Thin layers of cerium dioxide ($\text{CeO}_2$) have been prepared by various methods such as electrodeposition [7–9], hydrothermal [10], ion beam-assisted deposition [11], laser chemical vapor deposition [12–14], microwave-assisted heating [15], precipitation [16, 17], magnetron sputtering [18, 19], and sol–gel [20] methods. $\text{CeO}_2$ has salient characteristics such as oxygen buffer layers, high dielectric constant, and distinctive photocatalytic and optical properties, which allows its diverse applications in direct methanol fuel cells [21–23], direct alcohol fuel cells [24], proton exchange membrane (PEM) fuel cells [25, 26], solid oxide fuel cells [27], and solar cells [28], humidity and chemical sensors [29–31], dye-degradation [32], and sunscreen cosmetics [33]. Cerium oxide with a cubic fluorite structure in the reduced state has two charge states of $\text{Ce}^{3+}$ and $\text{Ce}^{4+}$, resulting in oxygen vacancies which contribute to large oxygen storage capacity [34, 35]. Properties of nanocrystalline $\text{CeO}_2$ were reported to be different from those of microcrystalline counterpart in ionic conductivity and chemical reactivity [36].

In this work nanocrystalline $\text{CeO}_2$ layers of various thicknesses were prepared on titanium by electrodeposition in isobutanol of three concentrations of $\text{Ce}^{3+}$ ions at 31.6 V, similarly to nanocrystalline lanthanum oxide and lanthanum oxycarbonate layers prepared at much higher voltages ranging from 200 to 1000 V [37]. Three concentrations of $\text{Ce}^{3+}$ ions used in the electrodeposition were 0.046, 0.092, and 2.0 mg/mL and currents were monitored during the electrodeposition. Deposition times ranged from 0.5 to 8 h. The as-prepared layers were then calcined at 700 K for 30 min. The morphology and composition of the deposition layers were examined by scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). Effects of electrodeposition concentration and time
on morphology of calcined layers and electrodeposition efficiency were investigated. Concurrently, structural data for as-prepared and calcined layers of nanocrystalline CeO_2 were deduced.

2. Experimental Details

Cerium nitrate hexahydrate (Ce(NO_3)_3·6H_2O, ≥99.0%, Fluka) powder was dissolved in a minimal amount of distilled water and further in isobutanol. The aqueous-organic mixture was evaporated by heating above 94°C to its nearly dried state, whose composition was examined by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha spectrometer) with an Al Kα microfocused monochromator. The dried cerium nitrate precursor was dissolved in isobutanol and the resulting solutions with concentrations of Ce^{3+} ions of 0.046, 0.092, and 2.0 mg/mL, corresponding to 0.33, 0.66, and 14.5 mM, respectively, were used in the electrodeposition.

The electrodeposition was carried out at room temperature in a cell which was made of Teflon and used in the previous study [37]. The electrodeposition area was 3.14 cm² and the distance between the electrodes was 10 mm. The cell was filled up to 3.5 mL with the organic cerium nitrate solution. Polished titanium foils were used as anodes and cathodes whose typical thickness was 11.4 μm. The titanium electrodes were washed consecutively by nitric acid, distilled water, and ethanol before being assembled into the cell. Voltage of the electrodeposition performed at room temperature was 31.6 V. The electrodeposition times of each concentration were 0.5, 2, 4, 6, and 8 h. The currents were monitored during the deposition time. Layers of deposited cerium oxide were washed consecutively by distilled water and ethanol. After being washed they were kept in ethanol for 24 h in order to remove the residual nitrate electrolyte and dried for 12 h in a drying oven at 50°C. The electrodeposited layers were calcined at 700 K for 30 min. Figure 1 shows the steps involved for syntheses of CeO_2 layers.

Morphology and surface compositions of electrodeposition layers were examined by scanning electron microscopy (SEM, Hitachi S-4300) and X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha). Their corresponding compositions and structural data with average crystalline sizes were determined from measurements by X-ray diffraction (XRD, PANalytical X’pert PRO MPD) with wavelength of Cu Kα, 1.5405 Å.

3. Results and Discussion

XPS spectrum of the cerium nitrate precursor with isobutanol dried on a Ti foil is shown in Figure 2(a). XPS spectra of electrodeposited layers are shown in Figures 2(b) and 2(c) which were obtained as prepared and calcined at 700 K for 30 min, respectively. Figure 2(a) shows photoelectron peaks of bulk Ce 3d, 4p, and 4d, O 1s, and C 1s along with Ti 2p arising from a titanium foil. The N 1s, O 1s, and C 1s peaks were due mainly to nitrate and isobutanol. Any significant impurities were not found in the cerium nitrate precursor. Figures 2(b) and 2(c) show photoelectron peaks of Ce 3d, 4p, and 4d, O 1s, and C 1s and their corresponding elemental compositions are listed in Table 1. As shown in Figures 2(b) and 2(c) and Table 1, the carbon and oxygen contents in the layers decreased after calcination.

The Ce 3d_{5/2} and 3d_{3/2} peaks with their corresponding satellite peaks in Figure 2 are expanded over the binding energy range of 925–875 eV in Figure 3. The Ce 3d_{5/2} main peaks for the cerium nitrate precursor and two layers in Figure 3 are at 882.9, 882.8, and 882.8 eV, respectively, while their corresponding 3d_{3/2} peaks are at 900.2, 901.3, and 901.2 eV, respectively. The Ce 3d peaks for the layers in Figures 3(b) and 3(c) match well within 0.1 eV, implying that they have the same chemical composition regardless of the calcination. The separation between Ce 3d_{5/2} and 3d_{3/2} peaks in the layers with or without calcination is 18.4–18.5 eV and the corresponding separation in the cerium nitrate precursor
Table 1: Elemental composition (atomic %) obtained from XPS spectra for cerium nitrate precursor and electrodeposition layers.

<table>
<thead>
<tr>
<th>Major element* (atomic %)</th>
<th>Cerium nitrate precursor</th>
<th>Layers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As-prepared</td>
<td>Calcined at 700 K for 30 min</td>
</tr>
<tr>
<td>Ce</td>
<td>4.6</td>
<td>13.0</td>
</tr>
<tr>
<td>O</td>
<td>61.9</td>
<td>52.6</td>
</tr>
<tr>
<td>C</td>
<td>20.3</td>
<td>32.3</td>
</tr>
<tr>
<td>N</td>
<td>13.2</td>
<td>2.1</td>
</tr>
</tbody>
</table>

*Titanium excluded in elemental compositions.

Figure 2: XPS spectra of (a) cerium nitrate precursor dried on Ti and layers on Ti electrodeposited at 31.6 V (b) as prepared and (c) calcined at 700 K for 30 min.

Figure 3: XPS spectra of Ce 3d peaks with their satellite lines denoted as S for (a) cerium nitrate precursor and the layers (b) as prepared and (c) calcined at 700 K for 30 min in Figure 2.

Figure 4: X-ray diffraction patterns of (a) cerium nitrate precursor dried on Ti and electrodeposition layers on Ti (b) as prepared and (c) calcined at 700 K for 30 min.

A wide-angle X-ray diffraction (XRD) pattern of the cerium nitrate precursor with isobutanol dried on a Ti foil is shown in Figure 4(a). XRD patterns of electrodeposition layers are shown in Figures 4(b) and 4(c), which were obtained as prepared and calcined at 700 K for 30 min, respectively. Figures 4(a)–4(c) show hexagonal Ti with crystal faces of (100), (002), (101), (102), and (110) due to Ti cathode foils. The as-prepared layer in Figure 4(b) shows diffraction peaks at 2θ = 28.4°, 32.8°, 47.2°, and 56.3°, which amount to (111), (200), (220), and (311) reflections of the cubic structure of CeO₂ (JCPDS card number 34-0394). The calcined layer in Figure 4(c) shows diffraction peaks at 2θ = 28.5°, 33.0°, 47.4°, 56.3°, and 59.2°, which amount to (111), (200), (220), (311), and (222) reflections of the cubic CeO₂. There are no traces of diffraction peaks of Ce₂O₃ in Figures 4(b) and 4(c), implying that the nanoparticles in the as-prepared and calcined layers were mainly CeO₂. The average crystallite size was estimated using Scherrer equation [17, 20, 37–39]:

\[ D = \frac{K \lambda}{\beta \cos \theta} \]  

where \( D \) is the average crystallite size, \( K \) is the dimensionless shape factor whose typical value is about 0.9, \( \lambda \) is the X-ray wavelength used in XRD (Cu Kα = 1.5405 Å), \( \beta \) is the broadening of the observed diffraction line at half the maximum intensity in radians, and \( \theta \) is the Bragg angle. The average crystallite sizes of the as-prepared and calcined layers
were estimated using (1) and concurrently structural data such as lattice parameter, dislocation density, strain, stacking fault, and texture coefficient were estimated and listed in Table 2.

<table>
<thead>
<tr>
<th>CeO₂ sample</th>
<th>hkl</th>
<th>Scherrer size (nm)</th>
<th>a (Å)</th>
<th>δ (nm⁻²)</th>
<th>Strain</th>
<th>SF</th>
<th>TC</th>
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</thead>
<tbody>
<tr>
<td>As-prepared</td>
<td>111</td>
<td>3.630</td>
<td>5.441</td>
<td>0.07587</td>
<td>0.00955</td>
<td>0.01983</td>
<td>1.1899</td>
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<tr>
<td></td>
<td>200</td>
<td>4.146</td>
<td>5.439</td>
<td>0.05817</td>
<td>0.00836</td>
<td>0.01628</td>
<td>0.8344</td>
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<tr>
<td></td>
<td>220</td>
<td>4.049</td>
<td>5.451</td>
<td>0.06098</td>
<td>0.00856</td>
<td>0.01432</td>
<td>1.1136</td>
</tr>
<tr>
<td></td>
<td>311</td>
<td>3.175</td>
<td>5.424</td>
<td>0.09918</td>
<td>0.01092</td>
<td>0.01714</td>
<td>0.8622</td>
</tr>
<tr>
<td>Calcined at 700 K for 30 min</td>
<td>111</td>
<td>6.991</td>
<td>5.428</td>
<td>0.02046</td>
<td>0.00496</td>
<td>0.01029</td>
<td>1.1364</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>8.494</td>
<td>5.426</td>
<td>0.01386</td>
<td>0.00408</td>
<td>0.00792</td>
<td>0.9499</td>
</tr>
<tr>
<td></td>
<td>220</td>
<td>6.572</td>
<td>5.420</td>
<td>0.02315</td>
<td>0.00527</td>
<td>0.00880</td>
<td>1.0453</td>
</tr>
<tr>
<td></td>
<td>311</td>
<td>6.612</td>
<td>5.420</td>
<td>0.02287</td>
<td>0.00524</td>
<td>0.00823</td>
<td>0.8685</td>
</tr>
</tbody>
</table>

SEM micrographs of CeO₂ layers obtained by 0.5 or 8 h electrodeposition with 0.046, 0.092, and 2.0 mg/mL of Ce³⁺ ions and subsequent 30 min calcination at 700 K are shown in Figure 5. The CeO₂ layers of the 30 min electrodeposition in Figures 5(a), 5(c), and 5(e) contain agglomerates with sizes ranging from 7 to 73, 7 to 94, and 7 to 146 nm, respectively, indicating that the sizes of agglomerates increase as the concentration of Ce³⁺ ions increases. At the 8 h electrodepositions in Figures 5(b), 5(d), and 5(f), the sizes of agglomerates increase to 209, 251, and 262 nm, respectively. The sizes of calcined CeO₂ agglomerates increased at higher concentrations and longer electrodeposition times even though the typical sizes of the corresponding as-prepared CeO₂ particles were measured from their SEM data to be in the vicinity of 4 nm regardless of the concentration and deposition time.

Currents of 0.5, 2, 4, 6, and 8 h electrodepositions at 31.6 V with 0.046, 0.092, and 2.0 mg/mL of Ce³⁺ ions are shown in Figures 6–10, respectively. Figure 6 shows that the currents of 0.5 h electrodepositions at 0.046, 0.092, and 2.0 mg/mL increase from 27 to 50, 32 to 62, and 356 to 643 μA, respectively. In Figure 7, the currents of 2 h electrodepositions at 0.046 and 0.092 mg/mL increase from 26 to 90 and 51 to 132 μA, respectively, while the corresponding currents at 2.0 mg/mL increase gradually from 367 to 768 μA for 65 min and slowly to 783 μA for 30 min and slowly decrease to 741 μA. In Figure 8, the currents of 4 h electrodepositions at 0.046 and 0.092 mg/mL increase with minor variations from 53 to 133 and 58 to 144 μA, respectively, while the corresponding currents at 2.0 mg/mL increase gradually from 388 to 739 μA for 45 min, decrease slowly to 645 μA for 75 min, increase sharply to 803 μA for 5 min, and then decrease slowly to 613 μA with some fluctuations. In Figure 9, the currents of 6 h electrodeposition at 0.046 mg/mL increase from 60 to 109 μA for 260 min and slowly decrease to 88 μA with minor variations, and those at 0.092 mg/mL slowly increase from 64 to 90 μA for 160 min, then increase sharply to 208 μA and drop to 176 μA for 5 min, and decrease slowly to 161 μA, while those at 2.0 mg/mL increase sharply from 303 to 467 μA for 25 min, decrease to 409 μA for 20 min, then increase to 468 μA after 20 min, decrease gradually to 319 μA for 65 min, and remain steady. Figure 10 shows that the currents of 8 h electrodepositions at 0.046, 0.092, and 2.0 mg/mL increase with minor variations from 68 to 127, 110 to 250, and 272 to
Table 3: Thicknesses and yields of electrodepositions for three concentrations of Ce$^{3+}$ ions.

<table>
<thead>
<tr>
<th>Deposition time (h)</th>
<th>Concentration of Ce$^{3+}$ ions (mg/mL)</th>
<th>0.046</th>
<th>0.092</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Thickness (mg/cm$^2$) Yield (%)</td>
<td>Thickness (mg/cm$^2$) Yield (%)</td>
<td>Thickness (mg/cm$^2$) Yield (%)</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.015 ± 0.014 24 ± 22</td>
<td>0.021 ± 0.015 17 ± 12</td>
<td>0.16 ± 0.02 5.7 ± 0.9</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.057 ± 0.010 91 ± 16</td>
<td>0.050 ± 0.014 40 ± 11</td>
<td>0.40 ± 0.04 15 ± 1</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.067 ± 0.015 106 ± 25</td>
<td>0.090 ± 0.019 72 ± 15</td>
<td>0.43 ± 0.03 16 ± 1</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.054 ± 0.022 86 ± 35</td>
<td>0.099 ± 0.018 78 ± 15</td>
<td>0.42 ± 0.03 15 ± 1</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.067 ± 0.062 106 ± 40</td>
<td>0.150 ± 0.036 120 ± 29</td>
<td>0.35 ± 0.03 13 ± 1</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5: SEM micrographs of CeO$_2$ layers calcined at 700 K for 30 min after (a) 30 min electrodeposition of 0.046 mg/mL of Ce$^{3+}$ on Ti, (b) 8 h electrodeposition of 0.046 mg/mL of Ce$^{3+}$, (c) 30 min electrodeposition of 0.092 mg/mL of Ce$^{3+}$, (d) 8 h electrodeposition of 0.092 mg/mL of Ce$^{3+}$, (e) 30 min electrodeposition of 2.0 mg/mL of Ce$^{3+}$, and (f) 8 h electrodeposition of 2.0 mg/mL of Ce$^{3+}$.

314 $\mu$A, respectively. The higher concentrations of Ce$^{3+}$ ions induced the higher currents due to the increase of cerium ions.

Thicknesses and yields of 0.5, 2, 4, 6, and 8 h electrodepositions at 31.6 V with 0.046, 0.092, and 2.0 mg/mL of Ce$^{3+}$ ions are shown in Figures 11–13 and Table 3, respectively. The yields of 0.5, 2, and 4 h electrodepositions at 0.046 mg/mL in Figure 11 are ∼24, ∼91, and ≥100%, respectively. Their corresponding thicknesses were 0.015, 0.057, and 0.067 mg/cm$^2$, respectively, implying that the deposition efficiency was highest at 0.5 h deposition and sharply decreased after 2 h. The yields of 0.5, 2, 4, 6, and 8 h electrodepositions
at 0.092 mg/mL in Figure 12 and Table 3 are 17, 40, 72, 78, and ≥100%, respectively. Their corresponding thicknesses were 0.021, 0.050, 0.090, 0.099, and 0.150 mg/cm², respectively, implying that the deposition efficiency was highest at 0.5 h deposition. Figure 13 shows that the yields of 0.5, 2, 4, 6, and 8 h electrodepositions at 2.0 mg/mL are 6, 15, 16, 15, and 13%, respectively. Their corresponding thicknesses were 0.16, 0.40, 0.43, 0.42, and 0.35 mg/cm², respectively, implying that the deposition efficiency was highest at 0.5 h electrodeposition as observed at the lower concentrations. The deposition efficiency was highest at 0.5 h deposition at all three concentrations. The 0.5 h electrodeposition at the highest concentration is suitable for preparation of thicker layers of cerium dioxide.

Similar results for XPS and XRD of as-prepared samples were observed irrespective of currents and deposition times. Typical particle sizes of as-prepared and calcined cerium dioxide samples shown in the corresponding SEM data were 4 and 7 nm, respectively, regardless of their concentrations, indicating that nucleation was driven mainly by the applied potential. However, the deposition time affected the size of calcined agglomerates, showing that longer deposition times increase the corresponding sizes.
Layers of CeO$_2$ nanoparticles with thicknesses ranging from 0.021 to 0.43 mg/cm$^2$ were prepared on titanium by electrodeposition with isobutanol solution and subsequent calcination. As-prepared and calcined deposited layers turned out to be cubic CeO$_2$. The average crystallite size increased from 4 to 7 nm through calcination at 700 K for 30 min irrespective of the concentration and the current. Structural parameters such as lattice parameter, dislocation density, strain, and stacking factors were reduced by the calcination. The deposition time affected the size of calcined agglomerates as longer deposition times increased the corresponding sizes.

The electrodeposition efficiency was highest at 0.5 h deposition at all three concentrations. The 0.5 h electrodeposition at the highest concentration is suitable for preparation of thicker layers of cerium dioxide, which are to be used in the investigation of cross sections of $^{142}$Pr produced in the proton-induced reaction with cerium.

**Conflicts of Interest**

The authors declare that they have no conflicts of interest.

**Acknowledgments**

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**References**


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