Electrochemical Synthesis of Zirconium n-Butoxide

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ABSTRACT
Zirconium n-butoxide was successfully synthesized using electrochemical method and characterized by IR and 1H-NMR spectra. The influence of various factors on the cell voltage of electrosynthesis process was studied. The cell voltage increased with an increase of electrode distance and current density, but decreased with the increasing Bu₄NBr concentration and solution temperature. The ideal conditions for electrosynthesis of zirconium n-butoxide were obtained. The resulting zirconium n-butoxide solution was purified by distillation and n-hexane extraction. Infrared spectra conformed to chemical bonds excellently, and the peak area ratio of nuclear magnetic resonance coincided with number ratio of hydrogen atoms in Zr(OC₄H₉)₄. The purity was close to 99.99%.

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Keywords : Zirconium Butoxide, Electrochemical Synthesis, Purification, Cell Voltage

1. Introduction
Zirconium oxide is a promising candidate for storage capacitors in dynamic random access memories, gate oxides in field effect transistors, antireflection layers for solar cells and photoprotective agents for wood due to its high dielectric constant, high refractivity and stable photochemical properties. Several methods are available to prepare zirconium oxide film such as chemical vapor deposition (CVD), ionized physical vapor deposition, and atomic layer deposition. Among these, CVD is the most promising method because it provides good step coverage, low probability of defective films, the possibility of deposition of films on substrates with large areas, and low damage to substrates. Zirconium alkoxide serves as an important precursor for preparation of zirconium oxide film.

The common route to synthesize zirconium alkoxide is based on zirconium tetrachloride with ethyl formate and dry ammonia. The process has the disadvantage that HCl gas is liberated, leading to severe corrosion of reaction apparatus. And the reaction is performed using large amounts of organic solvents which have to be costly disposed of. In addition, the necessary reagents are scarce, and the reactions involve multistep processes and are accompanied by various side processes which contaminate the products and decrease their yields.

Electrochemical dissolution of metals in absolute alcohols with a supporting electrolyte seems a promising synthesis method of metal alkoxides due to simplicity and high productivity as well as its continuous and non-polluting character. In 1972, the electrochemical synthesis of Ti, Ta, Si alkoxides was patented. In 1975, Lehnkuhl et al. synthesized a series of metal alkoxides under the same principle. Niobium, zirconium and hafnium alkoxides were also electro.synthesized by Berezkin et al. and Turevskaya et al. Electrochemical synthesis followed by vacuum distillation could prepare high-purity tantalum ethoxide. In Russia, this technique has been successfully employed for the commercial production of alkoxides of Y, Ti, Zr, Nb, Ta, Mo, W, Cu, Ge and Sn.

When zirconium oxide is used as an electronic material for dielectrics, it is necessary to reduce the impurity such as transition metals, alkali metals, alkaline earth metals as well as uranium and hafnium as far as possible. As far as we know, these impurity elements cause various disorder, increase the leakage of current and software errors. Despite the extensive study of electrochemical synthesis of zirconium n-butoxide, to the author’s knowledge, the synthesis conditions were chosen empirically, and the data on the effect of various factors on the electrolysis were almost absent. In the present work, zirconium n-butoxide was successfully synthesized using electrochemical method, the influence of various factors on the electrosynthesis process and the distillation-extraction purification of zirconium n-butoxide were also studied, which could provide technical guidance for the small scale production of high purity zirconium n-butoxide.

2. Experimental
2.1 Electrosynthesis of zirconium n-butoxide
A zirconium plate was supplied by Shenzhen Huahui Platinum Nonferrous Metal Co. Ltd., China with a chemical composition (wt%): S 0.0005, Al 0.0065, Fe 0.006, Si 0.0013, Mo 0.0002, Ni 0.0002, Cr 0.0009, Hf 0.0096, W 0.002, Pd 0.002, Nb 0.001, Nd 0.005 and Zr balance. The quatermary ammonium salts such as tetrabutylammonium bromide (Bu₄NBr), tetrachloroethylammonium chloride (Et₄NCl) and tetraethylammonium bromide (Et₄NBr) were purchased from Jintan Huadong Chemical Research Institute of Jiangsu Province, China. All reagents were used without further purification. A DC power source (ADD-12015D) and a distillation equipment were supplied by Shanghai Wenkai Power Equipment Co., Ltd. and Shenyang Shiboda Instrument Co., Ltd., respectively.

Bu₄NBr was selected as supporting electrolyte unless otherwise specified in the paper. Anhydrous n-butanol solutions containing 0.04–0.16 M supporting electrolyte were electrolyzed in a self-made cell (9.8 × 7.1 × 24.8 cm) without separating cathodic and anodic spaces. The cell was equipped with a reflux condenser, a zirconium plate (20 × 6 × 1 cm) anode and a stainless steel plate (22.3 × 8.1 × 0.2 cm) cathode. The whole system was sealed to avoid contact with moisture. Prior to each electrolysis, the electrodes were successively abraded with a series of emery papers, degreased with acetone, rinsed with deionized water and ethanol, dried and weighted for use. The electrolysis was performed under direct current with refluxing of the electrolyte at the anode. Hydrogen was evolved at the cathode. The electrosynthesis route is as follows.

Anode: Zr + Br⁻ + 3C₄H₉OH

→ Zr(OC₄H₉)₄Br + 4e⁻ + 3H⁺ (1)
other metal alkoxides with a low boiling point such as Fe(OC₄H₉)₃, n-hexane was distilled out under a pressure of 26000 Pa at 60°C and electrolyte. Zirconium n-butoxide went into n-hexane phase. Then solution was extracted using n-hexane to separate supporting electrolyte. When the gas phase temperature began to decrease, the distillation was stopped and the remaining n-butanol was distilled out at 88°C. When the gas phase temperature in the condenser began to be recorded using a thermometer inserted in the middle part of three-necked flask when the liquid drop began to drip from the bottom of condenser. The thermometer inserted in the middle part of three-necked flask.

3.1 Effect of supporting electrolytes

Figure 1 shows cell voltage-time curves for zirconium plate at a constant current density of 100 A/m² for 24 h in anhydrous n-butanol containing 0.08 M supporting electrolytes. Whether the supporting electrolyte was Bu₄NBr, Et₄NCl or Et₄NBr, the cell voltage decreased sharply in the early stage of electrolysis, then began to stabilize and finally increased slowly. When the electrolysis was performed, the rapid increase of solution temperature, and the dissolution of the oxide film grown on the zirconium surface gave rise to the sudden decline of cell voltage. The increase of cell voltage at later stage could be ascribed to two facts. First of all, an increase of the electrode distance and a gradual decrease of effective area as the electrolysis proceeded caused the increase of solution resistance. On the other hand, the increase of zirconium n-butoxide concentration and partial volatilization of n-butanol as the solution temperature rose, the solution viscosity was enhanced, impeding the migration and diffusion of the species, which also led to an increase of cell voltage. It was also observed that the stability of Bu₄NBr was superior to that of Et₄NCl and Et₄NBr, because the cell voltage began to increase when the electrolysis was sustained for 11 h for the former, longer than that for the latter. Under the same conditions, the cell voltage of zirconium in the anhydrous n-butanol containing Et₄NCl was the highest, followed by Bu₄NBr, and Et₄NBr was the lowest, indicating the conductivity of Et₄NBr and Bu₄NBr was superior to that of Et₄NCl. The current efficiency of zirconium in the anhydrous n-butanol containing different supporting electrolytes under the same conditions is listed in Table 1. The current efficiencies for these electrolytes decreased in the order: Bu₄NBr > Et₄NCl > Et₄NBr. All the current efficiencies were a little higher than 100%, which might be related to low valence state of zirconium in the electrolysis process. The reasons for this phenomenon require further study. According to the author’s knowledge, Et₄NBr is a strong oxidant, which is unfavourable to the stability of the electrolyte solutions. Considering several factors such as energy consumption, current efficiency and chemical stability of supporting electrolyte, Bu₄NBr was selected as supporting electrolyte.

3.2 Effect of Bu₄NBr concentrations

The cell voltage-current density curves for various Bu₄NBr concentrations are presented in Fig. 2. At the same concentration, the cell voltage was basically linear to current density. On the other hand, at the same current density, the higher Bu₄NBr concentration, the lower cell voltage. Cell voltage (\(E_I\)) can be expressed as the sum of theoretical decomposition voltage (\(E_d\)), overpotential (\(E_o\)), voltage drop of solution resistance (\(E_{R_s}\)) and external resistance (\(E_R\)) as follows.

\[
E_I = E_d + E_w + E_{R_s} + E_R
\]

where

\[
E_{R_s} = DI/k
\]

D, I, k is the current density, the electrode distance and the conductivity of solution, respectively. Equation (5) indicates that \(E_{R_s}\) linearly increases with current density. Usually, the theoretical decomposition voltage is constant for a fixed electrolyte, and \(E_o\) increases linearly with current density. Our previous study showed that \(E_o\) also increased linearly with current density when the overpotential was high.  Therefore, the linear relationship between

### Table 1. Current efficiency for different electrolyte types.

<table>
<thead>
<tr>
<th>Electrolyte types</th>
<th>Current efficiency/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bu₄NBr</td>
<td>103.55</td>
</tr>
<tr>
<td>Et₄NCl</td>
<td>101.56</td>
</tr>
<tr>
<td>Et₄NBr</td>
<td>101.52</td>
</tr>
</tbody>
</table>

Electrochemistry, 85(1), 2–6 (2017)
current density and cell voltage can be obtained. In addition, the higher Bu₄NBr concentration, the higher conductivity, leading to the lower cell voltage. From the energy saving point of view, a higher Bu₄NBr concentration was desirable. However, a higher Bu₄NBr concentration increased the difficulty of subsequent treatment. The Bu₄NBr concentration of 0.08 mol/L was preferable.

3.3 Effect of electrode distance

Figure 3 illustrates the cell voltage-current density curves for various electrode distance at a current density of 100 A/m² for 6 h at 70°C.

3.4 Effect of solution temperature

The cell voltage of zirconium in anhydrous n-butanol solution containing 0.08 M Bu₄NBr under various temperature is shown in Fig. 4. As can be seen, the cell voltage decreased with an increase of solution temperature. The conductivity of n-butanol containing supporting electrolytes was enhanced at a higher temperature. According to the Eq. (5), the cell voltage declined with an increase of conductivity, thus the cell voltage declined with temperature. In order to avoid volatilization of n-butanol, the electrolysis was performed at 65–70°C.

3.5 Effect of electrolysis time

Figure 5 displays the cell voltage curve of zirconium electrolyzed for 64 h under different time in anhydrous n-butanol solution containing 0.08 M Bu₄NBr. The cell voltage decreased sharply from 39 V to 19.5 V at 3 h, and then reached the minimum value 19 V at 7 h, finally increased to 50.2 V at 64 h. Similar results were obtained by Berezkin et al. and Yang et al.16,21 The increase of cell voltage with time at later stage might be associated with the exfoliation of zirconium powders. It was noticed that plenty of black powder appeared at the surface of the zirconium plate after a long-term electrolysis, which was later confirmed to be Zr by EDS (not shown here). Based on comprehensive consideration of cell voltage, current density and desired yield, electrolysis for 12–48 h was reasonable. When current density was high, the heat generated by electrolysis was serious, causing the increase of n-butanol consumption. So the current density of 100 A/m² was appropriate for the electrosynthesis of zirconium n-butoxide.
The morphology of zirconium plate before and after electrolysis is given in Fig. 6. The surface of the former was smooth and dim with some microcracks. On the contrary, the surface of the latter was very rough, with metallic luster and obvious etch pit, indicating pitting corrosion occurred on the surface of zirconium during the electrosynthesis.

### 3.6 Puriﬁcation of products

Zirconium n-butoxide was synthesized using electrosynthesis-puriﬁcation. Reduced pressure distillation-extraction is the preferable way for puriﬁcation of the crude zirconium n-butoxide solution. The n-butanol was evaporated under reduced pressure distillation, the curve of gas phase temperature and time is shown in Fig. 7. When the gas phase temperature reached 88°C under a pressure of 26000 Pa, a liquid drop began to drip and the temperature was recorded. The gas phase temperature initially kept stable with time until 6 h, and then increased to reach the maximum 183°C at 11 h. Finally, the gas phase temperature decreased. The gas phase temperature was associated with the distillation rate of n-butanol. When n-butanol was nearly distilled off at later stage, the temperature began to decrease. Due to the high boiling point, zirconium n-butoxide and supporting electrolyte remained in the solution. Then the resulting solution was puriﬁed by n-hexane extraction followed by distillation to get pure zirconium n-butoxide. The preparation conditions and main results are listed in Table 2. The impurity contents in the puriﬁed zirconium n-butoxide is listed in Table 3. The product of 29.68 g was obtained from the crude solution of zirconium n-butoxide, which was obtained by electrolysis through the charge amount of 14.00 Ah. The overall yield of zirconium n-butoxide was 56.27%. The purity was close to 99.99%, which can satisfy the demand of electronic material. The high content of Al and Hf in the product was due to the fact that zirconium n-butoxide has the close boiling point with alkoxides of Al and Hf. The yield is calculated based on the mass of ﬁnal zirconium oxide. The low yield was attributed to three reasons. First of all, a small part of zirconium n-butoxide did not enter into n-hexane phase in the extraction. The second was that some part of zirconium n-butoxide may be distilled out during separation of other alkoxides. The third results from the loss of zirconium n-butoxide during the whole puriﬁcation, hydrolysis and roasting process.

### 3.7 IR and 1H-NMR spectrum of products

Figure 8 shows FTIR spectrum of zirconium n-butoxide. As can be seen, there was no absorption bands in the region of 3600–3200 cm⁻¹ corresponding to hydroxyl group, indicating the product didn’t hydrolyze and had no n-butanol. The absorption bands at 2960–2800 cm⁻¹ were attributed to C-H stretching vibrations, and the peaks at 2960 and 2850 cm⁻¹ were attributed to asymmetric and

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**Table 2.** Preparation conditions and results of zirconium n-butoxide.

<table>
<thead>
<tr>
<th>Zirconium consumption (g)</th>
<th>Bu₄NBr concentration (mol/L)</th>
<th>Electrode distance (cm)</th>
<th>Electric quantity (Ah)</th>
<th>Mass of zirconium n-butoxide (g)</th>
<th>Temperature for n-butanol distillation (°C)</th>
<th>N-hexane consumption (mL)</th>
<th>Temperature for n-hexane distillation (°C)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.88</td>
<td>0.08</td>
<td>1.2</td>
<td>14.00</td>
<td>29.68</td>
<td>88</td>
<td>200</td>
<td>60</td>
<td>56.27</td>
</tr>
</tbody>
</table>

**Table 3.** Impurity contents of Zr(OC₄H₉)₄/×10⁻⁴%.

<table>
<thead>
<tr>
<th>Al</th>
<th>Cr</th>
<th>W</th>
<th>Hf</th>
<th>Si</th>
<th>Ni</th>
<th>Mo</th>
<th>Fe</th>
<th>Nb</th>
<th>Pd</th>
<th>Nd</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>29.4</td>
<td>3.7</td>
<td>0.7</td>
<td>57</td>
<td>0.5</td>
<td>1.2</td>
<td>1.1</td>
<td>0.4</td>
<td>0.9</td>
<td>1.6</td>
<td>3.2</td>
<td>0.4</td>
</tr>
</tbody>
</table>

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**Figure 6.** The morphology of zirconium plate before (a) and after (b) electrolysis.

**Figure 7.** The curve of gas phase temperature with time under pressure of 26000 Pa.

**Figure 8.** FTIR spectrum of zirconium n-butoxide.
symmetric stretching vibrations of CH$_3$, respectively. The peaks at 2930 and 2800 cm$^{-1}$ were assigned to asymmetric and symmetric stretching vibrations of CH$_2$, respectively. The peaks at 1460 and 1380 cm$^{-1}$ were attributed to C-H bending vibrations. The peak at 1260 cm$^{-1}$ was attributed to C-H twisting vibration. The absorption bands at 1090–1020 cm$^{-1}$ were assigned to C-O and C-C stretching vibrations. The peak at 418 cm$^{-1}$ was assigned to terminal Zr-O stretching vibration. The results were consistent with that of previous study.23

Figure 9 shows $^1$H-NMR spectrum of zirconium n-butoxide. The peak at 7.27 × 10$^{-6}$ was assigned to residual hydrogen in CDCl$_3$. The peak at 0.92 were assigned to C-O and C-C stretching vibrations. The peaks at 6.1 were assigned to terminal Zr-O (Color online) $^1$H-NMR spectrum of zirconium n-butoxide. Figure 9.

### 4. Conclusions

Zirconium n-butoxide was successfully synthesized by anodic dissolution of zirconium plate in anhydrous n-butanol with Bu$_4$NBr as supporting electrolyte. The resulting zirconium n-butoxide was purified by distillation followed by n-hexane extraction. The influences of process parameters on the electrosynthesis process were studied. Results showed that cell voltage decreased sharply in the early stage of electrolysis, and then began to stabilize in middle stage, finally increased gradually. Under the same conditions, the stability of Bu$_4$NBr was superior to that of Et$_4$NCl and Et$_4$NBr, respectively. The peaks at 1460 and 1380 cm$^{-1}$ were attributed to C-H bending vibrations. The peak at 7.27 × 10$^{-6}$ was due to terminal H$_3$. The peak at 1.38 × 10$^{-6}$ was due to bridging H$_2$. The peak at 1.58 × 10$^{-6}$ was due to bridging H$_2$, and the major peak at 3.99 × 10$^{-6}$ was attributed to H$_2$. The ratio of spectral integral area was 3:2:2:2, conforming to the stoichiometry of the compound Zr(OC$_4$H$_9$)$_4$.

### Acknowledgments

This work was supported by National Nature Science Foundation of China (Grant No 51374254), Innovation Project of Central South University for Graduate Students (Grant No 2016zzts275) and Teacher Research Foundation of Central South University in China (Grant No 2013JJSJJ026).

### References