Influence of Water on Passivation of Zr in n-butanol Solution Containing Bu$^\text{n}$4NBr

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ABSTRACT

To understand the role of water on zirconium passivation in n-butanol solutions containing Bu$^\text{n}$4NBr, composition and corrosion properties of the passive film were studied using cyclic voltammetry, X-ray photoelectron and electrochemical impedance spectroscopy. Zirconium undergoes spontaneous passivation followed by pitting corrosion as a result of passivity breakdown by the aggressive attack of bromide anions. The passive film consists mainly of ZrO$_2$, ZrO$_2$·2H$_2$O and a small amount of zirconium butoxide. The pitting potential shifts positively and pitting corrosion is seriously inhibited with the addition of a small amount of water. Water improves the pitting corrosion resistance of the passive film by changing the thickness and the relative ratio of OH$^-$/O$^2$$^-$. The result is helpful to electrosynthesize zirconium butoxide with high energy efficiency.

Keywords : Passive Film, Zirconium, n-Butanol, Water Content

1. Introduction

Zirconium oxide has been widely applied in industries due to its high dielectric constant, high refractivity and stable photochemical properties. It is usually prepared by chemical vapor deposition of zirconium alkoxide. Electrochemical dissolution of metals in absolute alcohols containing a supporting electrolyte has been proved to be a promising synthesis method of metal alkoxides. Many researchers synthesized tantalum, zirconium and titanium alkoxides using this method. It is well known that most metals especially valve metals are easy to undergo spontaneous passivation in anhydrous alcoholic solutions due to the formation of a protective oxide layer. The key to this technique is to break the oxide film and accelerate the metal dissolution. Palladium and Elayaperumal found that aggressive ions can break the protective film and induce pitting corrosion of zirconium. It is reported that the water content and alcohol molecular size in the anhydrous alcoholic solution also have great effects on the stability of passive film. However, less attention has been paid to the passive film generated on zirconium immersed in butanol solutions with or without water, especially the composition and corrosion property of the passive film. Furthermore, the passivation mechanism of zirconium in butanol solutions remains uncertain. Thus, it is necessary to clarify the real effect of water content on the zirconium passivation behavior in butanol solutions.

It was found that Bu$^\text{n}$4NBr is a good supporting electrolyte due to high conductivity and solubility in n-butanol. This work contributes to an understanding of the passivation behavior of zirconium in butanol solutions containing Bu$^\text{n}$4NBr by studying the role of water. The electrochemical impedance behavior of zirconium immersed in butanol solutions and the composition of the in situ formed passive film were investigated as a function of water content. The results will be helpful to electrosynthesize zirconium butoxide with high current efficiency.

2. Experimental

2.1 Materials and electrolyte solution

The electrolyte solution was prepared using n-butanol (99.5%, Beijing J&K), tetrabutyl ammonium bromide (99.8% Bu$^\text{n}$4NBr, Shanghai Aladdin) and acetonitrile (99.9%, Beijing J&K). All chemicals were superdry grade and used without further purification. The water content is lower than 0.01 wt%. The standard solution employed was 0.08 M Bu$^\text{n}$4NBr, 90% n-butanol and 10% acetonitrile by volume as solvent. Different amounts of water, i.e., 0.1 vol%, 0.5 vol%, 1 vol% and 2 vol% were added into this standard solution.

Electrochemical experiments were carried out in a conventional three-electrode glass electrochemical cell. A zirconium rod as working electrode (5.0 mm diameter, 20 cm long) was supplied by Zhuzhou Cemented Carbide Group Corporation, with a chemical composition (wt%): O 0.02, C 0.005, N 0.003, Fe 0.005, Si 0.0013, Mo 0.005, Ni 0.005, Cr 0.0009, Hf 0.0096 and Zr balance. The electrode was mounted in epoxy resin with an apparent exposed area of 0.19 cm$^2$. The counter electrode was a platinum foil (about 2 cm$^2$). All potentials were measured and reported relative to a saturated calomel electrode (SCE). An electrolyte filled bridge with a Luggin capillary was used to minimize the IR drop.

2.2 Electrochemical measurements

Electrochemical measurements were performed using CHI 660C electrochemical workstation (CH Instruments Inc, Shanghai) connected with a personal computer. Open-circuit potential ($\phi_{oc}$) was carried out on a freshly prepared electrode and the time was recorded when the electrode was immersed into the electrolyte solution. Cyclic voltammetry measurements (CV) were carried out by sweeping the potential from −1.1 V vs. SCE in the positive direction at a scan rate of 5 mV/s up to 4.0 V and then reversing with the same scan rate to the starting potential. Electrochemical impedance spectroscopy measurements were conducted at open circuit potential. The AC amplitude was 5 mV and the scanning frequency was controlled in the range from 0.01 Hz to 100 kHz. The experimental results were simulated based on the equivalent circuit using the Z-view program.

Prior to each experiment, the electrolyte solution was deaerated using ultra-pure nitrogen and then maintained under a nitrogen atmosphere throughout the whole process. The working electrode was successively abraded with a series of emery papers, from a coarse grade 600 to a fine grade 3600. After that, the electrode was rinsed with acetone, n-butanol, dried and finally dipped in the...
electrolytic solution. The electrode was allowed to corrode freely for a period of 1.0 h to obtain a steady state open circuit potential. In order to preclude the effect of water moisture in the air on electrochemical measurements, the preparation of zirconium electrode and electrolyte solution for the n-butanol solution without water was performed in a glove box.

2.3 XPS measurements
XPS samples were immersed in the electrolyte solution containing different amounts of water at 0.6 V vs. SCE for 15 min. The pretreatment of the sample is the same as electrochemical measurement except the lack of 1.0 h corrosion in the electrolyte solution. XPS measurements were performed using X-Ray photoelectron spectrometer ESCALAB 250Xi (ThermoFisher-VG Scientific). Photoelectron emission was excited by non-chromatic Al Kα radiation operated at 200 W.

3. Results and Discussion
3.1 Open-circuit potential
The plots of open-circuit potential ($\phi_{oc}$) versus time are shown in Fig. 1. It is observed that all the plots are quite similar. $\phi_{oc}$ quickly shifts toward positive potential at the beginning, then shifts slowly until it plateaus at 50 min, while $\phi_{oc}$ in the n-butanol solution without water has the largest positive shift within 60 min. This response indicates that spontaneous passivation occurs as a result of formation of oxide film on zirconium in all test solutions. Mogada reported that $\phi_{oc}$ increased with time for either mechanically polished or chemically etched zirconium electrode, which indicated oxide film thickening.18 Similar behavior for metal Ti in a methanol solution was also observed by Qin et al.17 The oxide passivation in an anhydrous n-butanol solution is possibly due to the presence of undissociated acid molecules, which undergoes decomposition on zirconium surface and provides oxygen.16,19 The addition of a small amount of water, as little as 0.1%, into the n-butanol solution seems to improve the protection characteristic of zirconium oxide. It is concluded that water participates in the formation of passive film and the stability of oxide film on zirconium in butanol solutions is strongly influenced by the water content. The stable $\phi_{oc}$ is much different among the solution with different water content, indicating that the composition and microstructure of the passive film is different.

3.2 Cyclic voltammetry curves
The cyclic voltammetry curves for Zr in n-butanol solutions containing different amounts of water are shown in Fig. 2.

As can be seen from the curves, there are no significant differences in the shape of the curves with different water contents. On the positive-going scan, zirconium does not exhibit active dissolution over a broad range of potential. The lack of active dissolution can be attributed to spontaneous passivation due to the formation of oxide film on zirconium surface, which shows agreement with the response of the open circuit potential with time.20,21 When the anodic potential exceeds a certain critical value, an abrupt increase of the current density is observed, which is due to the breakdown of the passive film and initiation of pitting corrosion. This critical potential is defined as pitting potential. When the potential is reversely scanned, the current density shows a continuous and small increase, typical of an autocatalytic character of pitting corrosion.22 Our previous study detected the occurrence of corrosion pits.23 After that, the current density begins to decrease and forms a hysteresis loop. When the water content is below 0.5%, an increase in water content shifts the pitting potential positively and the pitting corrosion above this potential is highly inhibited as indicated by a smaller current density. When the water content is greater than 0.5% the pitting potential and corrosion current show little dependence on water content. The initiation of pitting attack can be attributed to the adsorption of Br$^-\$ anions on the passive film and subsequent participation in the active dissolution to form soluble complex. Usually the passive film exhibits duplex nature with an external hydrated zirconium dioxide ZrO$_2$·nH$_2$O layer (amorphous or strongly defective) and an internal anhydrous ZrO$_2$ layer.10 It is deduced that water changes the passive film composition, microstructure and thickness, which decreases the affinity towards bromide ions as a result of occurrence of pitting corrosion at a more positive potential. The addition of 0.5% water is enough to form a layer of passive film. Further increasing the water content increases the thickness and fraction of hydrated zirconium dioxide of passive film. Thus, the pitting corrosion resistance is not improved when the water content is above 0.5%.

3.3 Electrochemical impedance spectroscopy
The impedance spectra and Bode phase angles for Zr immersed in n-butanol solutions with different water contents are presented in Fig. 3. It is seen that Nyquist plots for all solutions are similar and consist of an imperfect and depressed capacitive loop. The capacitive loop size decreases with an increase of water content, while the phase angle shows little dependence on the water content upon the presence of water. At high frequency, the phase angle tends to zero degree for all solutions, indicating that the impedance is
mainly dominated by the electrolyte resistance in this frequency region. At medium frequency, the maximum phase angle is around $-68^\circ$ for the water-containing solutions and $-55^\circ$ for the solution without water, indicating that water makes the passive film more like capacitive behavior.\cite{17, 18} But in all solutions, the phase angles are deviated from $-90^\circ$, indicating that the surface film is porous and defective. Figure 2 shows that the current density in the passive region is in the range of 30–90 µA/cm², while the passive current density for most metals with a tenacious passive film on the surface is 1–10 µA/cm².\cite{20, 22, 23} This result again shows that the passive film is defective. It may also be noted that the phase angle decreases significantly toward lower values at low frequency region, indicating that the impedance acts like a pure resistance of the surface film.

Many equivalent circuit models like one time constant, two time constants and two time constants accompanied by Warburg effects are chosen to fit the impedance data. It is found that the equivalent circuit shown in Fig. 4 shows the minimum fitting errors of parameters, where $R_1$ is the electrolyte resistance, $CPE$ and $R_2$ correspond to the capacitance and resistance of passive film, respectively. $C$ is a constant phase element related with the double layer capacitance. $R_1$ is the charge transfer resistance. $CPE$ is used to describe the distribution of a microscopic level by an empirical impedance function of the type:

$$Z_{CPE} = \frac{1}{j\omega C}\left(1 - j\frac{\omega}{\lambda}\right)^{-n}$$

(1)

Where $\omega$ is the angular frequency, $j^2 = -1$ the imaginary number and $n$ is the $CPE$ exponent, which reflects the deviation of capacitance from the ideal capacitive behavior. The value of 1 is characteristic for a capacitor, the value of 0 corresponds to a resistor and the value of 0.5 can be assigned to Warburg impedance.\cite{24}

The fitting data denoted by solid line in Fig. 3a show good agreement with the experimental data. The fitting results are listed in Table 1. It is observed that $R_1$ decreases from 316.3 to 183.1 Ω·cm² with the addition of a small amount of water, indicating that water improves the conductivity in the electrolyte solution. High values of $R_2$ and $R_3$ are observed in all solutions, which reflect the formation of a passive layer with high resistance to the charge transfer process. A slight increase in $R_2$ and $R_3$ with water content may be explained that the passive layer becomes thicker. The fluctuation of $CPE$ and $C$ can be interpreted that the composition of passive film changes with water content. Furthermore, surface concentration of water might be different from that in the bulk solution due to double-layer effects and solvation of dissolved metal ions.

3.4 XPS surface analysis

In order to determine the composition of the passive film with different water content, the passive film of Zr electrode was analyzed by XPS after immersion in n-butanol solutions at a potential of 0.6 V vs. SCE for 15 min. Figures 5 and 6 show the XPS spectra of binding energy regions of Zr 3d and O 1s on Zr surface. The Zr 3d spectra are similar in shape and the peak is decomposed into Zr 3d$_{5/2}$-Zr 3d$_{5/2}$ doublet. The spectrum can be fitted by six peaks of Zr 3d$_{3/2}$ and Zr 3d$_{5/2}$, which indicate the presence of three chemical states. As shown in Fig. 5(a) for the absence of water, the peak at 177.7 eV is assigned to Zr metallic state, the main peak at 182.0 eV is assigned to ZrO$_2$ and the peak at 180.0 eV is assigned to a new species Zr(OC$_4$H$_9$)$_4$. In our previous studies, it was found that Zr formed butoxide when reacting with n-butanol following reaction (2). Thus, a small amount of Zr(OC$_4$H$_9$)$_4$ may produce and leave on the surface of zirconium under this condition.\cite{9, 23} With the presence of water, the corresponding binding energy shows a little positive shift, indicating that water makes the oxide film more stable.

### Table 1. Values of fitted parameters of the equivalent circuit of pure Zr in n-butanol solutions.

| H₂O (%) | $R_1$ (Ω·cm²) | $CPE$ (Ω$^{-1}$·cm$^{-2}$) | $R_2$ (Ω·cm²) | $n$ | $C$ (Ω$^{-1}$·cm$^{-2}$) | $R_1$ (Ω·cm²) |
|---------|---------------|-----------------|---------------|-----|-----------------|---------------|
| 0       | 316.3         | $3.67 \times 10^{-2}$ | 9.01 $\times 10^4$ | 0.62 | 3.68 $\times 10^{-2}$ | 1.06 $\times 10^4$ |
| 0.1     | 249.5         | $2.96 \times 10^{-2}$ | 1.21 $\times 10^5$ | 0.78 | 3.82 $\times 10^{-2}$ | 1.28 $\times 10^5$ |
| 0.5     | 257.8         | $4.71 \times 10^{-2}$ | 1.33 $\times 10^5$ | 0.81 | 4.70 $\times 10^{-2}$ | 1.23 $\times 10^5$ |
| 1.0     | 183.1         | $3.28 \times 10^{-2}$ | 1.44 $\times 10^5$ | 0.82 | 3.03 $\times 10^{-2}$ | 1.38 $\times 10^5$ |
Zr + 4C4H9OH = Zr(OC4H9)4 + 2H2

(2)

Table 2 shows the relative atomic percentage of these three species with different water content. With the addition of 2.0% water, the ratio of ZrO2 to metal Zr increases from 29.7:1 to 50:1, indicating that water increases the thickness of passive film and reduces the porosity. Zirconium metal is an active metal and can react with water to form ZrO2 according to reaction (3). This result is consistent with electrochemical impedance spectroscopy.

Zr + 2H2O → ZrO2 + 2H2

(3)

Figure 6 shows that O1s band could be resolved into three peaks, which correspond to O2−, OH− and C-O, respectively, and that the relative amounts of these three species within the films varies with the water content as shown in Table 2. Figure 7 shows that a higher percentage of OH− groups is incorporated in the surface film with an increase of water content. It is recognized that a high vacuum required for the XPS measurement would have resulted in some dehydration of the film; hence the OH−/O2− ratio reported in Fig. 7 are unlikely to reflect the true ratio in the oxide film. Nevertheless, the general trend of the increasing OH− amount incorporated within the film with more water is believed to be valid. It is deduced that the passive film is mainly composed of ZrO2 and ZrO2·2H2O as well as a small amount of Zr(OC4H9)4. When the water is greater than 0.5%, the ratio of ZrO2·2H2O to ZrO2 shows an obvious increase, which again support the fact that water increases the thickness and the amount of hydrated zirconium dioxide of passive film. There is a compromise between the thickness and the amount of hydrated zirconium dioxide when the pitting corrosion resistance of passive film is considered.
Combining all the experimental results, the role of water in n-butanol solutions for Zr dissolution can be inferred. Zr has a very strong bond with oxygen atoms. C₂H₅OH molecules contain C-H, C-O, and O-H bonds, which all can be inserted with the Zr ion, and breaking of the C-H and O-H bonds are both exothermic reactions. Once Zr is exposed to n-butanol solutions, Zr begins to dissolve and forms zirconium butaoxide. The formation of Zr(OC₄H₉)₄ makes it clear that the favorable path is inserting the O-H bond. It is reasonable due to the chemical reactivity order: O-H > C-O > C-H. Compared with n-butanol, water molecules are much simpler, and contain only one kind of O-H chemical bond that can be inserted. Since the polarity of water is greater than n-butanol, water is more easily absorbed and reacts preferentially to form ZrO₂ and ZrO₂·H₂O. In the electrolysissynthesis of zirconium butaoxide, water in the electrolyte solution is removed as much as possible to get high current efficiency and low energy consumption.

4. Conclusions

Zirconium undergoes spontaneous passivation in n-butanol solutions followed by pitting corrosion as a result of passivity breakdown by the aggressive attack of bromide anions. The open circuit potential and pitting potential become more positive and pitting corrosion is seriously inhibited with increasing water content in the electrolyte to 0.5%. The passive film consists of ZrO₂·xH₂O and a small amount of Zr(OC₄H₉)₄. Water affects the pitting corrosion resistance by changing the thickness and relative ratio of OH⁻/O²⁻ of the passive film. Water in the electrolyte solution is removed as much as possible to get low energy consumption.

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References

1. C. M. Lopez, N. A. Suvorova, E. A. Irene, A. A. Suvorova, and M. Saunders, J. Appl. Phys., 98, 033506 (2005).
2. H. H. Zhang, C. Y. Ma, and Q. Y. Zhang, J. Inorg. Nucl. Chem., 83, 1311 (2009).
3. C. L. Dezelah, J. Niinistö, K. Kulki, F. Munnik, J. Lu, M. Ritala, M. Leskelä, and L. Niinistö, Chem. Vap. Depos., 14, 358 (2008).
4. M. Issue, H. Kominingamih, and T. I. Inui, Appl. Catal. A-General, 121, L1 (1995).
5. M. Y. Berezhkin, I. N. Chernykh, E. G. Polyakov, and A. P. Tomilov, Russ. J. Appl. Chem., 79, 741 (2006).
6. E. P. Turevskaya, N. I. Kozlova, N. Y. Turova, A. I. Belokon, D. V. Beredyev, V. G. Kessler, and Y. K. Grishin, Russ. Chem. Bull., 44, 734 (1995).
7. S. H. Yang, Y. M. Chen, H. P. Yang, Y. Y. Liu, M. T. Tang, and G. Z. Qiu, Trans. Nonferrous Met. Soc. China, 18, 196 (2008).
8. X. F. Zhou, A. B. Chu, and C. J. Lim, Electrochim. Acta, 47, 2769 (2002).
9. X. Y. Yang, J. F. Zhang, S. H. Yang, and H. Q. Huang, Electrochemistry, 85, 2 (2017).
10. A. S. Mogoda, Corrosion, 55, 877 (1999).
11. J. Banai, B. Stypula, K. Banai, J. Swiatowska-Mrowiecka, M. Starowics, and U. Lelek-Borkowska, J. Solid State Electrochem., 13, 1669 (2009).
12. J. A. Petit, G. Chatanier, and F. Dabosi, Corros. Sci., 21, 279 (1981).
13. H. F. Yang, S. H. Yang, Y. N. Cai, G. F. Hou, and M. T. Tang, J. Electrochem. Soc., 157, D168 (2010).
14. G. C. Palit and K. Elayarapuvel, Corrosion, 32, 276 (1976).
15. J. Swiatowska-Mrowiecka and J. Banai, Electrochim. Acta, 50, 1829 (2005).
16. U. Lelek-Borkowska and J. Banai, Electrochim. Acta, 47, 1121 (2002).
17. Z. Qin, X. Pang, L. Qiao, M. Khodayari, and A. Volinsky, Surf. Sci., 303, 282 (2014).
18. J. Banai, Mater. Sci. Forum, 185–188, 845 (1995).
19. S. P. Trasatti and E. Sivieri, Mater. Chem. Phys., 83, 367 (2004).
20. M. Amin, H. H. Hassan, and S. S. Abd El Rehim, Electrochem., 53, 2680 (2008).
21. Y. Y. Yang, H. Q. Huang, and S. H. Yang, Trans. Nonferrous Met. Soc. China, 26, 2738 (2016).
22. A. Amin, S. S. Abd El Rehim, and E. E. F. El Sherbini, Electrochem. Acta, 51, 4754 (2006).
23. Y. Y. Yang, L. Ran, and S. H. Yang, Electrochemistry, 84, 948 (2016).
24. H. Luo, H. Z. Su, C. F. Dong, and X. G. Li, Appl. Surf. Sci., 400, 38 (2017).
25. T. L. Yau, Mater. Corros., 43, 358 (1992).

Table 2. Atomic percentage of species containing O and Zr.

| Water content /% | species containing O /% | species containing Zr /% |
|-----------------|-------------------------|-------------------------|
|                 | O²⁻ | OH⁻ | C-O | ZrO₂ | Zr | Zr(OC₄H₉)₄ |
| 0               | 27.39 | 13.27 | 4.22 | 15.46 | 0.52 | 0.6 |
| 0.5             | 28.19 | 13.58 | 2.97 | 15.24 | 0.38 | 0.45 |
| 2.0             | 27.73 | 15.88 | 2.78 | 14.55 | 0.29 | 0.41 |

Figure 7. OH⁻/O²⁻ ratio as a function of water content.