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SnO₂-based gas (hydrogen) anodes for aluminum electrolysis

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Abstract: A novel SnO_2 -based gas anode was developed for aluminum electrolysis in molten cryolite at 850 °C to reduce energy consumption and decrease CO_2 emissions. Hydrogen was introduced into the anode, participating in the anode reaction. Carbon and aluminum were used as the cathode and reference electrodes, respectively. Cyclic voltammetry was applied in the cell to investigate the electrochemical behavior of oxygen ion on platinum and SnO_2 -based materials. The potential for oxygen evolution on these electrode materials was determined. Then, galvanostatic electrolysis was performed on the gas anode, showing a significant depolarization effect (a decrease of ~0.8 V of the anode potential) after the introduction of hydrogen, compared with no gas introduction or the introduction of argon. The results indicate the involvement of hydrogen in the anode reaction (three-phase-boundary reaction including gas, electrolyte and electrode) and give the possibility for the utilization of reducing gas anodes for aluminum electrolysis.

Key words: SnO₂-based gas anode; hydrogen anode; aluminum electrolysis

1 Introduction

Aluminum and aluminum alloys are very important materials for a wide range of applications in different areas such as transportation, construction and packaging. Primary aluminum was produced in the Hall-Héroult process, which was invented in 1886 [1]. In this process a consumable carbon anode is used which evolves CO₂ and must be adjusted and replaced periodically, resulting in disturbing the cell performance and increasing the corresponding energy consumption [1]. Because of the disadvantages of using a consumable carbon anode, nonconsumable (inert) anodes for oxygen evolution have been investigated during the last 40 years. When using inert anodes, the anode is dimensionally stable and the need to adjust and change the anode is eliminated. Thus, the whole cell has a more stable performance and decreased energy consumption is required. However, for aluminum electrolysis the theoretical cell voltage using a non-consumable anode is 2.2 V, which is about 1 V higher than that of a consumable carbon anode. Inert anodes with various materials (mostly $NiFe_2O_4$ and SnO_2 -based materials) have been investigated extensively in laboratory and pilot cells, but none of them have so far been successfully applied in aluminum electrolysis.

Gas anodes, which combine the advantages of carbon and inert anodes, have attracted more and more attention. Early in the 1960s, porous carbon was mainly used as the anode and a small depolarization effect was observed in molten cryolite for aluminum production [2–4]. In a US patent in 2000, a non-consumable anode of the type used for solid oxide fuel cells (SOFC) supplied with reformed natural gas was made for the aluminum electrolysis [5]. Later, several papers [6–8] reported the solid oxide membrane technology for producing metals from their oxides in molten salts, with the introduction of hydrogen. In addition, a nickel-based hydrogen diffusion anode was investigated in an experimental study of aluminum electrolysis, showing measurable depolarization of the anode potential in

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2011 [9].

Investigations on the gas anodes have not been carried out extensively. The main focus has been on porous carbon anodes and the type of SOFC with a zirconia-based solid membrane. They can be involved into the anode reaction or corrosion by the electrolyte. SnO₂-based materials are good candidates due to their low solubility in molten cryolite and good electrical conductivity. The authors have demonstrated the depolarization effects of Pt and SnO₂-based gas anodes in molten chlorides [10–13] and in molten cryolite [14]. In this work, hydrogen was introduced into SnO₂-based gas anodes during aluminum electrolysis to demonstrate the involvement of hydrogen in the anode reaction with the overall reaction shown below:

$$Al_2O_3 + 3H_2 = 2Al + 3H_2O$$
 (1)

The standard potentials for different electrode reactions (vs Al^{3+}/Al) in the system are shown in Table 1. The Gibbs energies for calculating the potentials in Table 1 were obtained by the thermodynamic software program HSC.

Table 1 Standard potentials for different electrode reactionsversus aluminum reference electrode in molten cryolitesaturated with alumina at $850 \,^{\circ}\mathrm{C}$

Electrode reaction	Standard potential/V
$Al^{3+}+3e=Al$	0
O ₂ +4e=2O ²⁻	2.28
$F_2+2e=2F^-$	4.60
$Sn^{4+}+O_2+4e=SnO_2$	2.86
$CO_2 + 4e = 2O^{2-} + C$	1.21
$H_2O+2e=O^{2-}+H_2$	1.32
$2HF+2e=2F^{-}+H_{2}$	1.31

2 Experimental

Stannex ELR blocks (Dyson Thermal Technologies) were used to prepare porous SnO₂-based anodes. The green body was a mixture of crushed blocks (Stannex ELR), screened to coarse grains of 180-355 µm, fine 96%SnO₂-2%CuO-2%Sb₂O₃ (mass fraction) powders and CMC as binder, which was rammed inside alumina tubes and then sintered at 1300 °C for 3 h. The fine ceramic powder mixture was used as binder phase during sintering to enhance the mechanical properties. In the designed SnO₂-based depolarized gas anode an inner steel tube for feeding gas was installed and surrounded concentrically by an outer steel tube with a bypass valve at the top, as shown in Fig. 1. The gases were introduced from the inner tube, which made the gases pass through the porous anode and into the electrolyte when the valve was closed.



Fig. 1 Schematic diagram of SnO₂-based depolarized gas anode

Na₃AlF₆ (natural cryolite, Greenland) and AlF₃ (Noralf, Boliden Odda AS) were mixed at the molar ratio of 1.59, and Al₂O₃ was added at a mass fraction of 4.5% (Merck, >99%). All the compounds were dried at 200 °C in air for at least 48 h. The system was operated at 850 °C and the electrolyte was saturated with alumina. The bottom of a carbon crucible lined with an alumina tube inside acted as the cathode (counter electrode). Both platinum (d=1 mm) (K. A. Rasmussen, Norway, 99.99%) and SnO₂-based materials were used as the working electrode for cyclic voltammetry and the latter was used as the anode for aluminum electrolysis. An Al³⁺/Al electrode was applied as the reference electrode. All the potentials in molten cryolite were referred to the aluminum reference electrode. The schematic of the electrochemical cell was described in Ref. [14].

The electrochemical measurements of the system were carried out by an Autolab potentiostat (PGSTAT 30) operating with GPES software (General purpose electrochemical system), with an upper limit of 1 A.

3 Results and discussion

Cyclic voltammetry was carried out using platinum SnO₂-based working electrodes in molten and Na₃AlF₆-AlF₃-Al₂O₃ at 850 °C. Platinum is a good material to be used to study the oxygen evolution in molten cryolite [15]. The cyclic voltammograms are shown in Fig. 2. On platinum wire the potential scan started from 1.75 to 2.4 V and then swept back. The reverse scan almost coincided with the initial one. At potentials negative to 2.3 V, the current was almost zero, indicating no occurrence of electrochemical reactions. From 2.3 V, the anodic current began to increase sharply. This value is close to the theoretical standard potential for oxygen evolution listed in Table 1, indicating that the large anodic current corresponds to oxygen evolution. XIAO [15] observed oxygen evolution at ~2.2 V with

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Fig. 2 Cyclic voltammograms on Pt wire and dense SnO_2 -based anodes in molten Na_3AlF_6 - AlF_3 - Al_2O_3 (4.5%) at 850 °C and scan rate of 10 mV/s

respect to aluminum in molten cryolite saturated with alumina at 1030 °C. Hence, oxygen evolution occurred at ~2.3 V in this system according to Reaction (2). In the molten electrolytes prepared in this work, O^{2-} represents the complex anions containing oxygen, e.g., $Al_2OF_6^{2-}$ and $Al_2O_2F_4^{2-}[1]$. The simplified anode reaction can be written as follows:

$$2O^{2^{-}}=O_{2}+4e$$
 (2)

During the initial scan on the dense SnO₂-based anode, there was almost no current before reaching 2.25 V. Then, the current increased until 2.8 V, which was the upper limit. Before oxygen evolution, expected to occur at 2.28 V theoretically according to Table 1, some residual current was observed. It might be due to the reduction oxidation reactions involving corrosion products from the SnO₂-based anode [15] since there was no residual current when platinum was used as the working electrode.

From the above results, the anode potential was controlled to be above 2.3 V (e.g., 2.4-3 V) in the constant current electrolysis while no gas was introduced to enable the occurrence of Reaction (2). Then, the designed SnO₂-based depolarized gas anode was tested with the introduction of hydrogen. Galvanostatic electrolysis was carried out in molten Na₃AlF₆-AlF₃-Al₂O₃ (4.5%) at 850 °C. Figure 3 shows the anode potential and cell voltage as function of time at an apparent current density of 0.1 A/cm². For 0<t<60 min, the anode potential was ~ 2.7 V, which was stable before the introduction of argon. When argon $(10 \text{ cm}^3/\text{min})$ was supplied, an instant decrease occurred and then the anode potential became stable. For 110 min<t<280 min argon was replaced by hydrogen. After 10 min, the anode potential decreased to 1.9 V gradually. At the same time the cell voltage went down to around 1 V. The lower levels for the anode potential and the cell voltage were maintained for around 40 min before increasing to higher values without changing the gas supply.



Fig. 3 Anode potential (a) and cell voltage (b) vs time during constant current electrolysis (0.1 A, 0.1 A/cm²) using SnO₂-based depolarized gas anode in molten Na₃AlF₆-AlF₃-Al₂O₃ (4.5%) at 850 °C

During the first 120 min, oxygen was formed according to Reaction (2). The instant decrease caused by the introduction of argon was likely due to the agitation. It was evident that the introduction of hydrogen led to a significant decrease of the anode potential. Compared to the introduction of argon, it was concluded that hydrogen was involved in the anode reaction, resulting in its depolarization effect according to Reaction (3).

$$O^{2-}+H_2=H_2O+2e$$
 (3)

The depolarization effect of hydrogen was observed with a decrease of anode potential and cell voltage by 0.8 V and 1 V, respectively, although the lower potential could not be maintained for a long time. It is not clear why the lower potential could not be maintained for a long time. It might be due to insufficient supply of O^{2-} or some barrier of hydrogen transfer to the three-phase boundary after some time, which needs to be further explored. In addition, some delay, of about 10 min, was observed from the introduction of hydrogen to a change in the anode potential, due to the fact that the distance from the gas reservoir to the anode is approximately 10 min at a flow of $10 \text{ cm}^3/\text{min}$.

The theoretical consumption of hydrogen during the constant current electrolysis at a current of 0.1 A was calculated as $2.9 \text{ cm}^3/\text{min}$ according to Reaction (3). In this electrolysis, the amount of supplied hydrogen is adequate for the complete occurrence of Reaction (3) theoretically.

From Table 1 the theoretical anode potential difference between Reactions (2) and (3) is around 1 V, which is consistent with the measured value, indicating that the electrochemically active sites for the three-phase-boundary Reaction (3) were successfully built. The three phases include O^{2^-} in molten cryolite, electrons from the solid anode and reducing gas from the gas phase.

At least two experiments were carried out to confirm the reproducibility of the depolarization effect of the reducing gas for aluminum electrolysis. The results are shown in Fig. 4. Figure 4(a) shows that after the



Fig. 4 Anode potentials vs time during constant current electrolysis under different conditions using SnO₂-based depolarized gas anodes in molten Na₃AlF₆–AlF₃–Al₂O₃ at 850 °C: (a) 0.1 A, 0.1 A/cm², 4.5% Al₂O₃; (b) 0.2 A, 0.2 A/cm², 4.3% Al₂O₃

introduction of hydrogen (10 cm³/min) the anode potential was found to decrease by around 0.8 V. In Fig. 4(b) the gas anode was also tested at a larger apparent current density of 0.2 A/cm². After the introduction of hydrogen with a flow rate of 10 cm³/min, the anode potential was decreased by 0.2 V. By increasing the hydrogen flow to 20 cm³/min, a further decrease of 0.4 V was observed. In this case the application of a larger current resulted in more hydrogen (20 cm³/min) needed to achieve an obvious depolarization effect.

4 Conclusions

1) In molten cryolite saturated with alumina, oxygen evolution on the platinum and the SnO₂-based anode was investigated and a residual current before the release of oxygen on the SnO₂-based anode was observed.

2) The depolarization effect of hydrogen was demonstrated during constant electrolysis at an apparent current density of 0.1-0.2 A/cm² on the designed SnO₂-based depolarized gas anodes. The decrease of the anode potential and cell voltage reach 0.8 and 1 V, respectively, which are close to the theoretical values.

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铝电解中二氧化锡基(氢气)气体阳极

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摘 要: 开发一种在低温电解质(850 °C)铝电解中应用的新型二氧化锡基气体阳极以降低铝电解能耗和二氧化碳 排放。在此种气体阳极中,氢气通入阳极后参与阳极反应,分别用石墨和铝作阴极和参比电极。采用循环伏安法 研究此体系中铂和二氧化锡基电极上氧离子的电化学行为,并确定氧气的析出电势。然后,采用气体电极进行恒 电流电解实验,相对于未通入气体和通入氩气,通入氢气后阳极出现明显的去极化现象(阳极电势约下降 0.8 V)。 实验结果表明,氢气已参与阳极三相界面(气体-电解质-电极)反应,为还原性气体阳极在铝电解上的应用提供了 可行性。

关键词: 二氧化锡基气体阳极; 氢气阳极; 铝电解

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