

Low-Melting $\text{CaCl}_2\text{-NaCl-Al}_2\text{O}_3$ Electrolyte for Direct Electrochemical Reduction Solid Al_2O_3

Hongwei Xie¹, Jinxia Wang², Yuchun Zhai^{*1}, Xiaoyun Hu³ and Chengde Li¹

¹School of Materials and Metallurgy, Northeastern University, Shenyang, 110819, China

²School of science, Northeastern University, Shenyang 110819, China

³Northeastern University Engineering Research Institute Co. Ltd, Shenyang 110013, China

Abstract: The electrical conductivity and density of the low-melting $\text{CaCl}_2\text{-NaCl-Al}_2\text{O}_3$ systems at 550°C~800°C ranges were respectively measured by the Continuously Varying Cell Constant Technique, ac-techniques and Archimedes method. The materials were applied as the electrolyte for the direct electrochemical reduction solid Al_2O_3 at 550°C~800°C. The materials were composed of 71wt.%~87wt.% CaCl_2 (corresponding NaCl), NaCl and Al_2O_3 (without and saturated). The results showed that additive Al_2O_3 decreased the electrical conductivity of the materials, and resulted in the increase of activation energy of conductance. The functional relationship between the electrical conductivity and temperature was linear, and conformed to the Arrhenius equation. Increasing the CaCl_2 content decreased the electrical conductivity of the materials, but the density was increased. Increasing the CaCl_2 , the decrease scope of the electrical conductivity was small and the increase trend of the density was slowed down, the influence of increasing the content of CaCl_2 in systems on the direct electrochemical reduction solid Al_2O_3 process is smaller. The temperature was a decisive factor on the electrical conductivity of the electrolytes and electrolysis process.

Keywords: Molten $\text{CaCl}_2\text{-NaCl-Al}_2\text{O}_3$ electrolyte system, electrical conductivity, density, low temperature, direct electrochemical reduction solid Al_2O_3 .

1. INTRODUCTION

It has been over a century since the establishment of the fundamentals of the Hall-Héroult process in electrolytic aluminium. The dissolved alumina is electrolyzed in the molten electrolytes. Cryolite is the dominant electrolyte material because of its unique capacity as a solvent for alumina. However, the cell temperatures always ranging between 940°C and 980°C because of the high melting point of cryolite. A lot of energy (15000kWh/t Al) and excellent carbon materials (500kg/t Al) are consumed [1-3].

It is always a hot point to seek a new low energy consumption method of aluminium production. Seeking the low melting point electrolyte materials is one of the most active researches for low temperature aluminium electrolysis. It can improve current efficiency, reduce anode carbon consumption and may also increase cathode life. Additionally, it can enhance the prospects for the developm

ent and introduction of inert anodes. Researchers have spent many years for this effort [4-8]. Unfortunately, it brings the problems of lower alumina solubility, electrolyte conductivity, and density differential between metal and electrolyte in any application. A solid cryolite 'crust' formed on the cathode surface when the molecular ratios and temperature of the electrolytes are decreased, which shows that little progress has been done in the present.

The recent development of a process for obtaining metals and alloys by direct electrochemical reduction of their respective oxides in CaCl_2 base fused salt electrolytes has stimulated significant scientific and industrial interest. Researchers have successfully prepared metals such as Ti, Si, Cr and so on [9-20]. In this case, it is not essential for the solid oxide to have high solubility in the molten salts because the solid oxides are not dissolved in the molten salt as ionic state, instead being used as the cathode to be directly reduced electrochemically. Therefore, there are more possibilities to choose low-melting electrolyte, which can make aluminium electrolysis at low temperatures feasible. Based on the previous work [21] measuring the electrical conductivity and density of the low-melting $\text{CaCl}_2\text{-NaCl-Al}_2\text{O}_3$ electrolytes offer data to low temperature direct electrochemical reducing solid Al_2O_3 in this paper.

2. EXPERIMENTAL

Materials.—Graphite (big crucible for fusing salts and electrolysis experiments: outer diameter 190mm, inner diameter 150mm, height 120mm, depth 100mm; small crucible for measuring density: outer diameter 60mm, inner diameter 50mm, height 100mm, depth 90mm; conductivity cell for measuring electrical conductivity: shown in Fig. (2) were purchased from Sinosteel Shanghai Advanced Graphite Materials Co. Ltd. Anhydrous CaCl_2 (AR), NaCl(AR) and Al_2O_3 (AR) powders were supplied by Tianjin Kermel Chemical Reagent Co. Ltd., Al-Mg alloy was obtained by mixing the metallic Al(90wt.%) and Mg.

All chemicals were dried at 400°C. All of graphitic products were dried at 150°C. Quantifying, mixing and

*Address correspondence to this author at the School of Materials and Metallurgy, Northeastern University, Shenyang, 110819, China; Tel: +86-024-83673860; Fax: +86-024-83687731; E-mail: xiehw@smm.neu.edu.cn, zhaiyc@smm.neu.edu.cn

filling of the chemical materials were carried in a glove box with argon (99.996%).

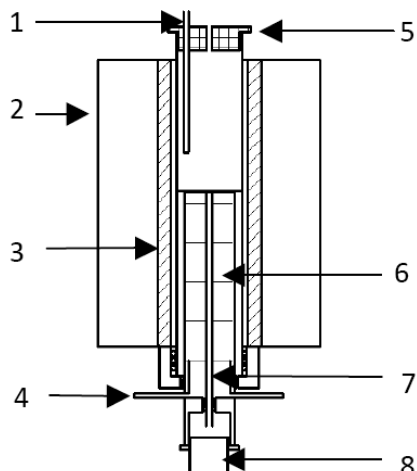


Fig. (1). Measurement equipment. 1 measuring temperature thermocouple, 2 furnace, 3 double whorl silicon-carbon tube, 4 inlet gas, 5 firebrick lid, 6 firebrick, 7 controlling temperature thermocouple, 8 auto-lift clutch.

Electrical Conductivity and Density Measurement

Equipment

A vertical furnace belonged to a compound measurement equipment was shown in Fig. (1), it was composed of a program control temperature instrument ($\pm 0.5^\circ\text{C}$), a heating conductor of double helix silicon carbon, Pt-Pt10Rh thermocouple; a program control lifter ($\pm 0.01\text{mm}$); and an electronic balance ($\pm 1\text{mg}$)

Melts Preparation

The mixed salts were contained with a big graphite crucible. At the highest experimental temperature, the mixed salts were melted in a sealed reactor and were stirred by a stirrer with a corundum top (40 r/min) to accelerate the Al_2O_3 dissolution. After stirring, the upper liquid of the melt was dumped into the measurement container. Then the container was placed in the vertical furnace. The graphite crucible contained surplus salts were replaced in the sealed reactor and temperature was steadied at the next experimental temperature. All measurements were controlled at Ar gas atmosphere (99.996%).

Electrical Conductivity

The measurement of the electrical conductivity was based on the CVCC technique and ac-techniques with a sine wave signal with small amplitude at a high frequency range [22-27]. Fig. (2) Was the cell which consisted of a graphite cover with a corundum tube 7 of inner diameter 5mm, outer diameter 6mm and length 100mm, a graphite crucible 9 of outer diameter 53 mm and height 120mm, which was used as one electrode. A tungsten rod 2, enclosed in a corundum tube 3 using high temperature resistant cement was the other electrode, which was fixed by the fixed arm. The length of cell was changed automatically by lifting and descending the vertical laboratory furnace.

A PGSTAT302N and a BOOSTER 20A were employed to measure the cell impedance. The amplitude was 10 mV, the frequency was varied from 100 Hz to 100 kHz, and 31

readings were taken within this range. A personal computer was used for controlling PGSTAT302N and BOOSTER 20A and to collect the data by Frequency Response Analysis software.

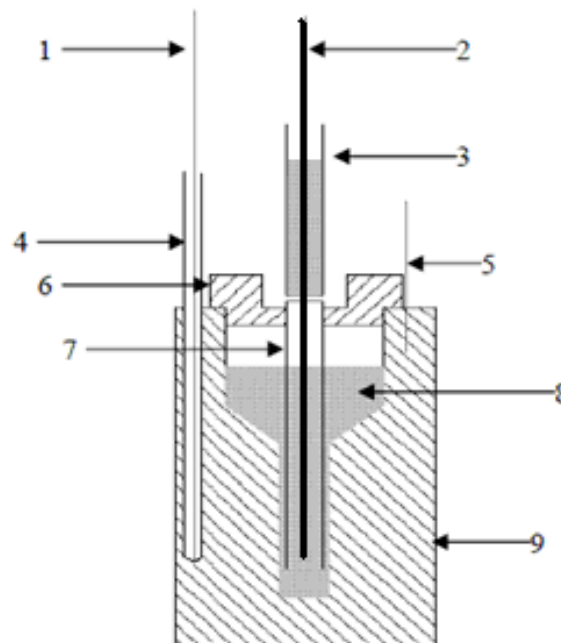


Fig. (2). Cross-section of the conductivity cell. 1 thermocouple, 2 tungsten electrode, 3,7 corundum tube, 4 thermocouple tube, 5 stainless steel contact rod, 6 graphite cover, 8 melt, 9 graphite crucible.

Density

The density was measured by Archimedes method [28]. The hammer and the thin chain for suspending hammer were metallic molybdenum materials. The measurements were carried out in the compound measurement equipment

Direct Electrochemical Reduction Solid Al_2O_3

Put dried CaCl_2 and NaCl (mol ratio 1: 1) into graphite crucible. As shown in Fig. (3) the solid Al_2O_3 powders were formed into the cathode by molding, and sintered at 1500°C and anode was installed and was inserted into molten salt. The reactor was sealed and then the pre-treatment to the mixed salts below its melting point was carried out, which is to further deprive H_2O and O_2 , followed by heating the mixed salt to melt. During this process, argon was injected to avoid oxidation. Afterwards, the pre-electrolysis was carried under the decomposing voltage of Al_2O_3 , which is to minimize the impact of the impurities.

After pre-electrolysis, the voltage was increased to constant 3.2V, until the current was kept around $0.1 \times 10^{-2}\text{A}$. The sketch of cell was showed in Fig. (3). Fig. (3a) was used under 650°C and Fig. (3b) was used over 700°C . After the electrolysis process, the cathode was taken out and then the metal and salt were separated by fusion.

RESULTS AND DISCUSSION

Electrical Conductivity

The electrical conductivity data in the molten system can be described by a simple equation of the Arrhenius type:

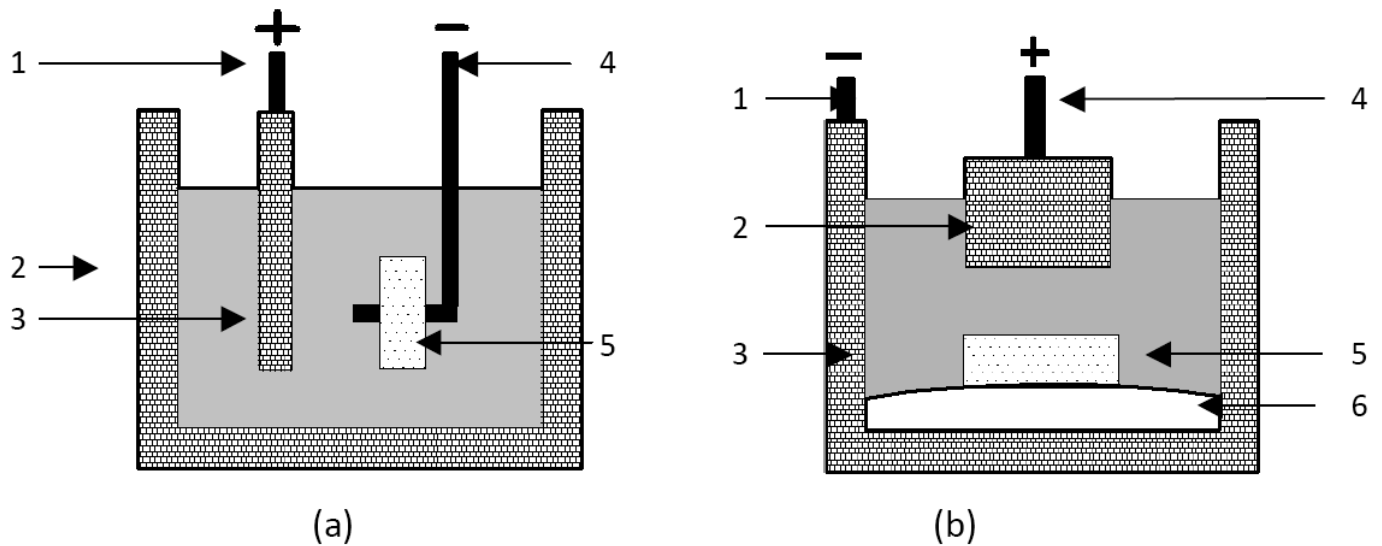


Fig. (3). Sketch of cell. (a) 1,4 wire, 2 graphite crucible, 3 graphite, 5 Al₂O₃; (b) 1,4 wire, 2 graphite, 3 graphite crucible, 5 Al₂O₃, 6 Al-Mg alloy.

$$\kappa = k_0 \exp(-E_a/RT) \quad (a)$$

where κ is the electrical conductivity in S/cm; k_0 is the coefficient related to chemical composition of melt; E_a is the activation energy of conductance, in J/mol; T is the temperature of the melt, in K; R is the universal gas constant, 8.314 J/(mol.K).

The logarithm form of Eq. (a) is

$$\ln \kappa = \ln k_0 - E_a/RT \quad (b)$$

when $\ln k_0 = A$, $-E_a/R = B$

$$\text{then } \ln \kappa = A + B/T \quad (c)$$

The cross-sectional area, A of the tube-type cell was known in molten CaCl₂ whose electrical conductivity was 2.02 at 800°C [29], that is $A = 0.14 \text{ cm}^2$.

The Systems CaCl₂-NaCl and CaCl₂-NaCl-Al₂O₃

The melt was composed of 71wt.%CaCl₂ and 29wt.%NaCl. The melt with saturated alumina was also used. The operating temperature ranged from 550°C to 750°C.

Fig. (4) shows the plots of the experimental conductivity data (each point represents an average value 6 runs) as a function of temperature. The functional relationship is linear, which conforms to the Arrhenius equation, dedicates that the particles of both systems are in ionic state. The electrical conductivity of system (2) lower than that of the system (1), shows that the addition of alumina lowers the electrical conductivity of the electrolyte.

The solid lines in Fig. (4) represent Eq. (c), the parameters A and B of this equation are given in Table 1. The activation energy of conductance of the system (2) has higher electrical conductivity than that of the system (1). However, the difference between both cases is small. Addition of alumina increases the activation energy of conductance in both cases; however, the influence is small.

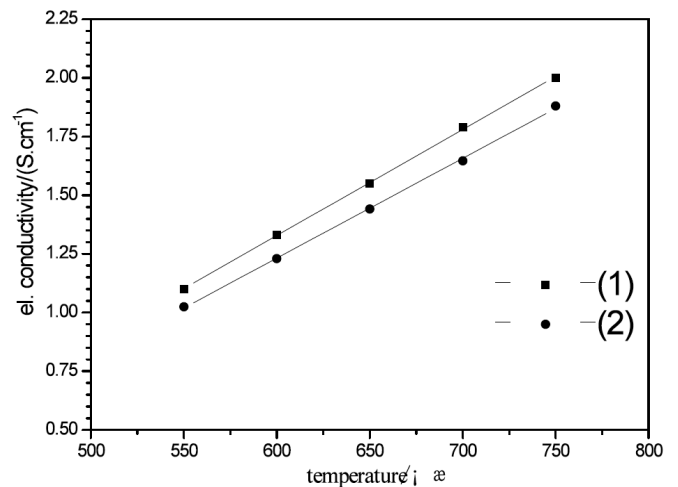


Fig. (4). Electrical conductivity of the CaCl₂-NaCl-Al₂O₃ systems as a function of temperature. The compositions: (1) 71wt.%CaCl₂, 29wt.%NaCl, (2) same melt plus alumina(saturated). Symbols: experimental data, fitting lines: Eq. (c).

The Systems CaCl₂-NaCl-Al₂O₃

The melts with saturated alumina were used. The content of the CaCl₂wt.% (corresponding NaCl) in the melts were (1)74%, (2)77%, (3)82%. The operating temperature ranged from 600°C to 800°C.

Fig. (5) shows plots of the experimental conductivity data (each point represents an average value 6 runs) as a function of temperature. The functional relationship is linear, which conforms to the Arrhenius equation. With the increase of the CaCl₂ content, the electrical conductivity correspondingly lowers in three cases. However, the differences between them are small, especially in both systems (2) and (3). The results are due to following several reasons. Firstly, the sodium chloride does not react with the calcium chloride to form compounds. Secondly, the crystal of sodium chloride is

Table 1. The Parameters A and B of the Eq (c) for the CaCl₂-NaCl-Al₂O₃ Systems

System CaCl ₂ -NaCl/(wt.%)	Additive Al ₂ O ₃	lnκ=A+B/T			E _a /(J.mol ⁻¹)	Temperature Range /°C
		A	B	Related Coefficient of Fitting		
71-29	0	3.1683±0.0521	-2523±48	0.99946	20975	550-750
71-29	saturated	3.1135±0.0229	-2540±21	0.9999	21117	550-750

typically ionic structure, however, that of calcium chloride is a transition structure between ionic structure and molecular structure. When they are fused, Sodium chloride has the ability to entirely decompose to form the simple Na⁺ and Cl⁻, however, calcium chloride should be decomposed with two steps:

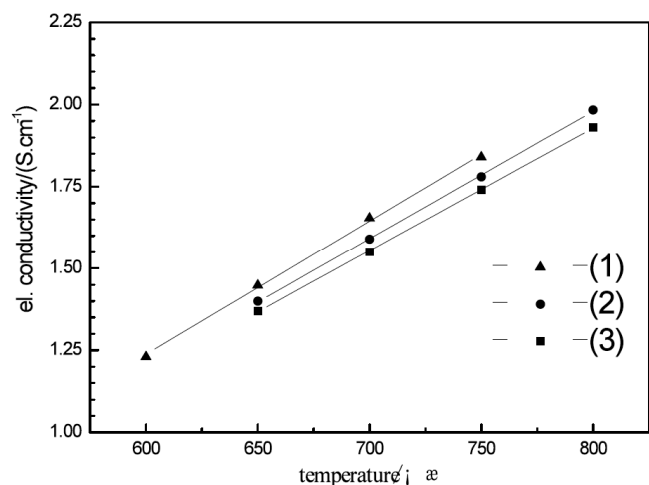


Fig. (5). Electrical conductivity of the CaCl₂-NaCl-Al₂O₃ systems with the saturated Al₂O₃ as a function of temperature. The compositions: (1) 74wt.%CaCl₂, 26wt.%NaCl, (2) 77wt.%CaCl₂, 23wt.%NaCl, (3) 82wt.%CaCl₂, 18wt.%NaCl. Symbols: experimental data, fitting lines: Eq. (c).



The step (d) is relatively thorough, however step (e) is carried partially. Thirdly the solubility of the oxides is lower in the chlorides, the influence of additive alumina on systems is small. The cationic conductives are mainly Na⁺ and a few of Ca²⁺ in the melts. In three systems, the concentrations of Na⁺ are gradually decreased with the increase of CaCl₂ content. The decrease of Na⁺ results in the decrease of the electrical conductivity. However, the increase of CaCl₂ moves the balance of the step (e) to right, the Ca²⁺ are increased. The increased Ca²⁺ prevent the cationic conductive from large amplitude decrease. So the decreased

amplitude of electrical conductivity of three melts is small.

The solid lines in Fig. (5) represent Eq. (c), the parameters A and B of this equation are given in Table 2. The activation energy of conductance is reduced with the increase of CaCl₂ content in the melts. The reasons are following: the volume of Ca²⁺ are bigger than that of Na⁺, the increase of Ca²⁺ content enlarges the motion space of Na⁺ in the melt. Therefore, the activation energy of conductance of the systems is decreased.

Density of the Systems CaCl₂-NaCl-Al₂O₃

The volume of the hammer was known in molten CaCl₂ whose density was 2.05g/cm³ at 800°C [30], that is V=2.36 cm³.

Fig. (6) shows plots of the density data (each point represents an average value 6 runs) as a function of CaCl₂ concentration in systems at three temperatures. The functional relationship is nonlinear. The density of the melts correspondingly increased with the increase of CaCl₂ content in the melts, however the trend is slow down. The density of the system a) at 550°C, 600°C and the system b) at 600°C are presented in Table 2.

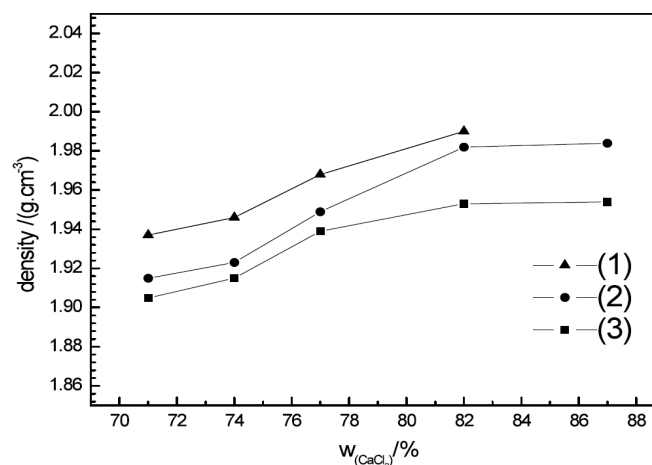


Fig. (6). Density of the CaCl₂-NaCl-Al₂O₃ systems as a function of the CaCl₂ concentrations at three temperatures: (1) 650°C, (2) 700°C, (3) 750°C.

Table 2. The Parametres A and B of the Eq (c) for the CaCl₂-NaCl-Al₂O₃ Systems (Al₂O₃ Saturated)

System CaCl ₂ -NaCl/(wt.%)	lnκ=A+B/T			E _a /(J.mol ⁻¹)	Temperature Range /C
	A	B	Related Coefficient of Fitting		
74-26	3.0576±0.1326	-2493±125	0.99749	20729	600-750
77-23	2.8229±0.0183	-2296±18	0.99994	19086	650-800
82-18	2.7706±0.0113	-2267±11	0.99998	18851	650-800

Direct Electrochemical Reduction Solid Al_2O_3

Fig. (7) shows the relationship between current and time during electrolysis in the $\text{CaCl}_2\text{-NaCl-Al}_2\text{O}_3$ (71wt.% CaCl_2 , 29wt.% NaCl) system at 550°C and 600°C. The currents gradually down with the time extended, but it is very evident that the electrolytic current at 600°C is bigger than that at 550°C. The results indicate that the temperature of the molten electrolyte system seriously affect on the direct electrochemical reduction solid Al_2O_3 process. Fig. (8) shows the relationship between current and time during electrolysis in different $\text{CaCl}_2\text{-NaCl-Al}_2\text{O}_3$ systems at 800°C. The currents are still gradually lower with the time extended, but the change between them is very small. The results indicate that the influence of the CaCl_2 content in the molten electrolyte on the direct electrochemical reduction solid Al_2O_3 process was smaller. It can be found that the number of currents in Fig. (8) are bigger than that of Fig. (7). It further indicates that the molten electrolyte temperature is relatively an important factor.

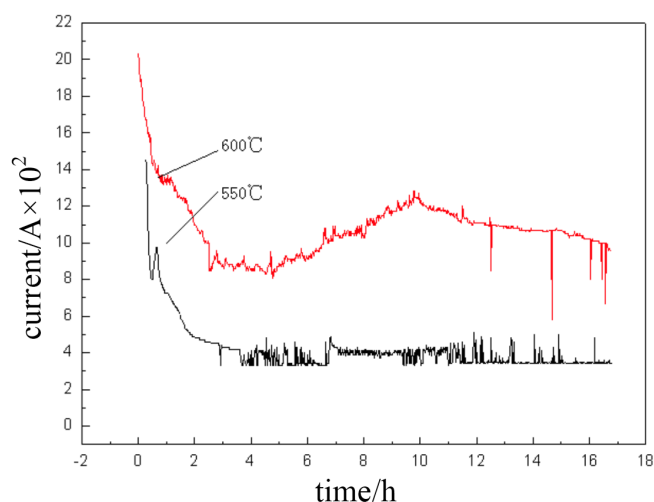


Fig. (7). Current/time curves of electrolysis at 550°C and 600°C.

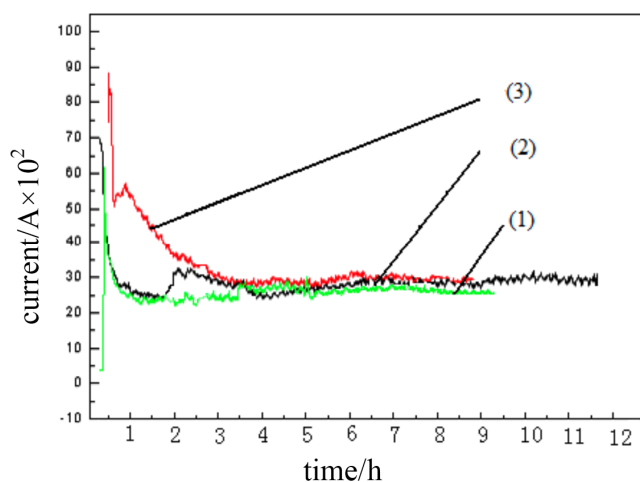


Fig. (8). Current/time curves of electrolysis at 800°C in different $\text{CaCl}_2\text{-NaCl-Al}_2\text{O}_3$ systems.

The cross-section photos of electrolytic Al_2O_3 cathode at 800°C showed in Fig. (9) the metallic luster can be saw. The XRD analysis result is shown in Fig. (10). The metallic Al phase character is detected.

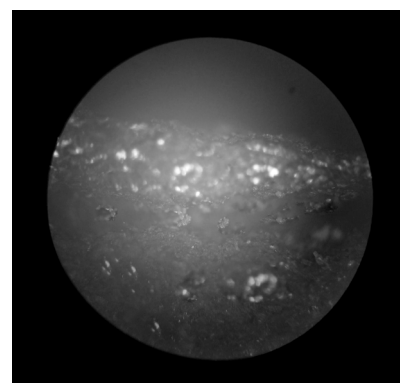


Fig. (9). The cross-section photo of electrolytic Al_2O_3 cathode under the microscope (10 ×).

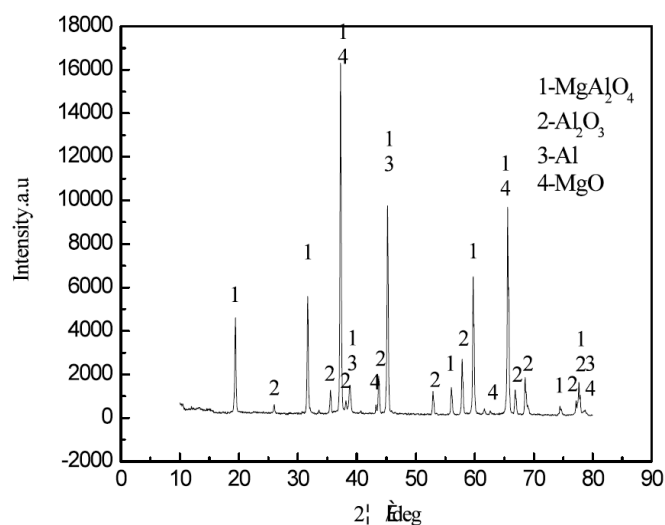


Fig. (10). XRD of electrolytic Al_2O_3 cathode.

3. CONCLUSIONS

Additive Al_2O_3 lowered the electrical conductivity of the $\text{CaCl}_2\text{-NaCl-Al}_2\text{O}_3$ systems, and resulted in the increase of the activation energy of conductance of the system. In experimental ranges, the functional relationship between the electrical conductivity and the temperature was linear, and conformed to the Arrhenius equation. Increasing the CaCl_2 content, the electrical conductivity of the systems was lowered, and the density was increased. The electrolysis experimental results indicated that the molten $\text{CaCl}_2\text{-NaCl-Al}_2\text{O}_3$ can be used as the electrolyte for direct electrochemical reducing alumina. The temperature was a decisive factor on the electrical conductivity of the electrolyte and directly and electrochemically reducing alumina in it.

ACKNOWLEDGMENTS

Financial support from the National Natural Science Foundation of China (Grant No.50674026) and the Fundamental Research Funds for the Central Universities (N100302008) are gratefully acknowledged.

REFERENCES

- [1] Sadoway DR. Inert anodes for the Hall-Héroult cell: The ultimate materials challenge. *JOM* 2001; 53: 34-5.
- [2] Kvande H, Haupin W. Inert anodes for Al smelters: Energy balances and environmental impact. *JOM* 2001; 53: 29-33.

- [3] Pawlek RP. Inert anodes: an update [C]//Light Metals 2002. Warrendale Pa: TMS 2002; 449-56.
- [4] Sleppy WC, Cochran CN. Bench scale electrolysis of alumina in sodium fluoride-Aluminum fluoride melts below 900°C. Aluminium 1979; 5: 604-6.
- [5] Grjotheim K, Kvande H. Physico-chemical properties of low-melting baths in aluminium electrolysis. Metall 1985; 39: 510-13.
- [6] Qiu ZX, Li QF, Ho MH. Aluminium electrolysis at lower temperature [C]//Light Metals 1985. Warrendale Pa: TMS 1985: 529-44.
- [7] Beck TR. Non-consumable metal anode for production of aluminum with low-temperature fluoride melts [C]//Light Metals 1995. Warrendale Pa: TMS 1995: 355-60.
- [8] Vecchio-Sadus AM, Dorin R, Frazer EJ. Evaluation of Low-temperature electrolytes for aluminium smelting. J Appl Electrochem 1995; 25: 1098-104.
- [9] Chen GZ, Fray DJ, Farthing TW. Direct electrochemical reduction of titanium dioxide to titanium in molten calcium chloride. Nature 2000; 407: 361-4.
- [10] Yan XY, Fray DJ. Using electro-deoxidation to synthesize niobium sponge from solid Nb₂O₅ in alkali-alkaline-earth metal chloride melts. J Mater Res 2003; 18: 346-56
- [11] Gordo E, Chen GZ, Fray DJ. Toward optimisation of electrolytic reduction of solid chromium oxide to chromium powder in molten chloride salts. Electrochim Acta 2004; 49: 2195-208.
- [12] Nohira T, Yasuda K, Ito Y. Pinpoint and bulk electrochemical reduction of insulating silicon dioxide to silicon. Nat Mater 2003; 2: 397-401.
- [13] Muir Wood AJ, Copcutt CR, Chen GZ, Fray DJ. Electrochemical fabrication of nickel manganese gallium alloy powder. Adv Eng Mater 2003; 5: 650-3.
- [14] Glowacki BA, Fray DJ, Yan XY, Chen GZ. Superconducting Nb₃Sn intermetallics made by electrochemical reduction of Nb₂O₅-SnO₂ oxides. Phys C Supercond Appl 2003; 387: 242-6.
- [15] Jin XB, Gao P, Wang DH, Hu XH, Chen GZ. Electrochemical preparation of silicon and its alloys from solid oxides in molten calcium chloride. Angew Chem Int Ed 2004; 43: 733-6.
- [16] Fenn AJ, Cooley G, Fray D, Smith L. Exploiting FFC Cambridge process. Adv Mater Process 2004; 162: 51-3.
- [17] Bossuyt S, Madge SV, Chen GZ, *et al.* Electrochemical removal of oxygen for processing glass forming alloys. Mater Sci Eng A 2004; 375-77, 240-3.
- [18] Chen GZ, Fray DJ. Voltammetric studies of the oxygen-titanium binary system in molten calcium chloride. J Electrochem Soc 2002; 149: E455-E467.
- [19] Flower HM. A moving oxygen story. Nature 2000; 407: 305-6.
- [20] Schwandt C, Fray DJ. The electrochemical reduction of chromium sesquioxide in molten calcium chloride under cathodic potential control. Z. Naturforsch 2007; 62: 655-70.
- [21] Xie HW, Zhang H, Zhai YC, Wang JX, Li CD. Al preparation from solid Al₂O₃ by direct electrochemical deoxidation in molten CaCl₂-NaCl at 550°C. Mater Sci Technol 2009; 25: 459-61.
- [22] Hiveš J, Thonstad J. Electrical conductivity of low-melting electrolytes for aluminium smelting. Electrochim Acta 2004; 49: 5111-4.
- [23] Fellner P, Kobbeltvedt O, Sterten Å, Thonstad J. Electrical conductivity of molten cryolite-based binary mixtures obtained with a tube-type cell made of pyrolytic boron nitride. Electrochim Acta 1993; 38: 589-92.
- [24] Chrenková M, Danek V, Silný A, Utigard TA. Density, electrical conductivity and viscosity of low melting baths for aluminium electrolysis[C]//Light Metals 1996. Warrendale Pa: TMS, 1996: 227-32.
- [25] Wang XW, Ray P, Alton T. Electrical conductivity of cryolitic melts [C]//Light Metals 1992. Warrendale Pa: TMS, 1991: 481-8.
- [26] Kim K B, Sadoway D R. Electrical Conductivity Measurements of Molten Alkaline-Earth Fluorides. J Electrochem Soc 1992; 139: 1027-33.
- [27] Kan HM, Wang ZW, Ban YG, Shi ZN, Qiu ZX. Electrical conductivity of Na₃AlF₆-AlF₃-Al₂O₃-CaF₂-LiF(NaCl) system electrolyte. Trans. Nonferrous Met Soc China 2007; 17: 181-6.
- [28] Wang CZ. Researching methods on physical chemistry of metallurgy. Metallurgical Industry Publishers Press: Beijing in China 1981.
- [29] Han W, Huo GZ, Gong CF, Li FX, Zhao GL, Eds. Electrolytic Method on Magnesium. Metallurgical Industry Publishers Press: Beijing in China 1981.
- [30] Xie G, Ed. Principle and application of molten salts metallurgical industry. Publishers Press: Beijing in China 1998.

Received: September 28, 2010

Revised: November 5, 2010

Accepted: December 21, 2010

© Xie *et al.*; Licensee Bentham Open.This is an open access article licensed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0/>) which permits unrestricted, non-commercial use, distribution and reproduction in any medium, provided the work is properly cited.