

ELECTROCATALYTIC BEHAVIORS OF CER ON SOME METAL OXIDES IN CHLORIDE MELT AT 700 °C^①

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ABSTRACT The polarization behaviors of various oxide electrodes prepared on graphite substrate by thermal decomposition procedure have been investigated by linear sweep voltammetry in chloride melt at 700 °C. Experimental results showed that some oxides have obvious electrocatalytic activity for chlorine evolution, lowering anodic overpotential up to 80 ~ 110 mV at a current density of 0.6 A/cm². The kinetic analysis of steady state *J-E* data in terms of Tafel slopes and chronocoulometric measuring inferred that the mechanisms of CER on RE oxide electrodes was atom + ion route, with Heyrovsky reaction ($\text{Cl}_{\text{ads}} + \text{Cl}^- \rightarrow \text{Cl}_2 + \text{e}^-$) being the rate-determining step, and the adsorption of intermediate species Cl_{ads} obeying non-activated Temkin condition.

Key words chlorine evolution reaction electrocatalysis chloride melt oxide electrode

1 INTRODUCTION

Electrochemical industry is in general a huge energy consumer. Electrocatalysis, as a powerful weapon in lowering overpotential, provides an available choice for saving energy. Electrocatalysis of CER in chloride melts is of special interest from the point of molten salt batteries and metal winning processes. Chlorine has been considered as a potential oxidant for fuel cell. Al/Cl₂ redox couple is a candidate electrochemical reaction for energy storage device. An important content in fuel cell study is to seek suitable materials active for CER. Early publishes were mainly concerned on this aim. Uchida *et al*^[1-6] had reported several papers concerning the performances of metal oxides in NaAlCl₄ (175 °C) and LiCl-KCl (450 °C) melt. They found that some noble metal oxides such as Ru₂O₃, Rh₂O₃ and IrO₂ demonstrated good electrocatalytic activity for CER. However the studies conducted by Uchida were limited to chloride melt with a low melting point. The temperature adopted in molten salts electrolytic metallurgy is normally above 650 °C. Whether there exists electro-

catalysis for CER at such a high temperature, what materials would be active for CER, and how much electrocatalysts could minimize the overpotential have not been reported up to now. In present paper, attempts are made to do primary investigation on electrocatalysis of CER in NaCl-KCl melt at 700 °C.

2 EXPERIMENTAL

Electrolytic vessel was a quartz container of 1100 mm × 250 mm. Inside was a quartz crucible of 500 mL. The temperature was kept at 700 ± 1 °C during experiment. Melt consisted of equimolar AR grade NaCl and KCl. The mixture was pre-dried at 120 °C for more than 24 h and then pre-electrolyzed in 2 mA/cm² current density for 24 h at 700 °C.

Oxide electrodes were prepared by thermal decomposition procedure on spectrum pure graphite substrates. Graphite rod, 6 mm in diameter, were polished with 200 grit sand paper, cleaned in supersonic device, degreased with acetone, boiled in HCl acid, calcined at 400 °C and washed thoroughly with distilled water. Pre-

① Project 59604005 supported by the National Natural Science Foundation of China

Received Jun. 23, 1998; accepted Dec. 18, 1998

pared oxide electrodes were sealed into quartz tube. No working part of electrode was insulated with sealant. Working electrode was designed as L-type structure. Counter-electrode was rectangular graphite plate.

Two types of reference electrodes, Ag/AgCl and bare Pt wire, were used. Melt compositions were AgCl (10 %) and equimolar NaCl and KCl (90 %). Bare Pt wire was used as a pseudo reference electrode^[7].

Electrochemical measuring was performed at 700 °C under nitrogen atmosphere. Prior to experiment, melt was pre-electrolyzed under 3 mA/cm² for 1 h with graphite electrodes. The position and depth of working electrode was kept constant each time.

Three-electrode system was used to measure the steady polarization curve. Improved current interruption technique was employed in the measurement of IR drop and anodic overpotential. Positive feedback IR compensation was applied in electrochemical transient measuring.

Instrument used was Model 273 potentiostat/galvanicstat of EG&G PARc. Controlling and sampling was performed via M270 electrochemical research software. Current interruption signal was produced by Model 273. Its rising time is 3 µs. Lecroy LS140 Digital Oscilloscope, whose bandwidth is 100 MHz and sampling rate 100 MS/s, was used to capture the wave variation at the instant of current interruption.

3 RESULTS AND DISCUSSION

3.1 Behaviors of CER on some transition metal oxides

Systematic investigation on chlorine electrode reaction was conducted in KCl-NaCl melt at 700 °C on: (1) oxides of Fe, Co, Ni, Cr, Mo, Sn, Mg and Ru; (2) spinel structural ($M_2M'O_4$) mixed oxides of Co + Mg, Co + Mn, Co + Fe, Co + Ni, Ni + Fe and Fe + Mg; (3) ferrite structural ($A_xFe_{3-x}O_4$) mixed oxides of $Co_{0.75}Fe_{2.25}O_4$ and $Ni_{0.85}Fe_{2.15}O_4$. The electrocatalytic activity was characterized by overpotential reducing^[8], which was obtained through measuring the polarization curves and comparing

the overpotential of oxide electrode with that of graphite electrode under identical condition and current density. Testing results indicated that $Co_{0.75}Fe_{2.25}O_4$ mixed oxide demonstrated good electrocatalytic activity on CER, as shown in Fig.1, lowering the anodic overpotential up to 80 mV at a current density of 0.6 A/cm². Calculated Tafel slope b and exchange current density J^0 was 137 mV and 0.041 A/cm² respectively. RuO_2 , transition metal oxides and mixed oxides investigated showed no obvious activity on CER. Mn oxide and Mo oxide even exhibited inactivity to CER as resistance rising in oxide layer.

Fig.1 Polarization curves of oxide electrodes

Transition metal species have unique unpaired d-electron and unfilled d-orbital which are available for forming bonds with adsorbates. They are expected to have electrocatalytic activity on electrode reaction with adsorption of intermediate. Contrary to this general concept, the behaviors of those species in chloride melt at high temperature were quite different from their performances in aqueous solution, especially for ruthenium oxide, which was proved to be excellent electrocatalyst for CER. Those results reflected the complication and particularity of molten salts. Possible reason responsible for this phenomenon may be that the corrosiveness of chloride at a high temperature makes the oxides layer easy to be dissolved chemically or

physically. The electrocatalytic properties of $\text{Co}_{0.75}\text{Fe}_{2.25}\text{O}_4$ may devote to the synergistic effect during the preparation of mixed oxide. The kinds and structure of mixed oxides vary widely, being potential electrocatalysts for CER.

3.2 Behaviors of CER on RE metal oxides

Rare earth metal and its oxides show many special physical and chemical properties as its unique 4f inner electron arrangement and movement characteristic, which make them become important candidates in developing new type advanced materials and electrocatalysts. Unfilled 5d-orbital in RE atoms provides available active sites for intermediate adsorbates during electrochemical reaction. The electronic structure of RE^{n+} ion makes oxides display semiconductor characteristics and good electrical properties at high temperature. Distinct properties make RE oxides become prospective electrocatalyst for CER at high temperature. Catalysts RE and its oxides have gained some applications in the field of chemical catalysis or electrocatalysis at low temperature^[9, 10].

Electrochemical measuring was performed in NaCl-KCl melt at 700 °C on the oxide electrodes of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Tm, Yb and Y. Typical anodic polarization curves were shown in Fig.1 to Fig.3. Overpotentials and their reducing values of 13 oxide electrodes in 0.6 A/cm² current density were listed in Table 1. Compared with graphite electrode, Pr, Tb and Tm oxides lowered anodic overpotential up to 80 ~ 110 mV, Dy, La, Y and Sm 70 ~ 80 mV, and Yb and Nd 50 ~ 60 mV. But, Ce, Gd, Eu and Er oxides showed inactivity to CER or surficial resistance increasing. The serial of electrocatalytic activity of RE oxides according to their anodic overpotential reducing was $\text{Pr} \geq \text{Tb} > \text{Tm} > \text{Dy} \geq \text{La} \geq \text{Y} \geq \text{Sm} > \text{Yb} \geq \text{Nd}$.

Besides overpotential reducing, Tafel slope and exchange current density are used as criteria for the evaluation of electrocatalytic activity. The polarization curves were converted into Tafel relationship, and the obtained Tafel parameters of RE oxide electrodes were listed in Table 2. Electrocatalytic properties characterized

by Tafel slope and exchange current density are in good agreement with data from overpotential measurement. A few exception may be ascribed to experimental errors.

Fig.2 Polarization curves of oxide electrodes



Fig.3 Polarization curves of oxide electrodes

Investigation on mixed RE oxides were carried out with (1) La + Co, La + Ni, La + Mn and La + Cr mixed oxides; (2) $\sum \text{RE}$ (La + Pr + Nd + Sm + Eu) + Co, $\sum \text{RE}$ + Ni, $\sum \text{RE}$ + Mn, $\sum \text{RE}$ + Cr and $\sum \text{RE}$ + Ru mixed oxides; and (3) Yb + Fe and Y + Fe mixed oxides. Testing results, as shown in Fig.3, showed that Ru and

Table 1 Overpotential of RE oxide electrodes in 0.6 A/cm² current density

Electrode	La	Ce	Pr	Nd	Sm	Gd	Tb	Dy	Tm	Yb	Y	Graphite
Overpotential/ mV	158	293	135	185	161	521	138	157	150	178	160	236
Overpotential reducing/ mV	- 78	57	- 101	- 51	- 75	285	- 98	- 79	- 86	- 58	- 76	0

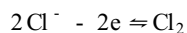
Table 2 Tafel slope and exchange current density of RE oxide electrodes

Electrode	La	Pr	Nd	Sm	Tb	Dy [*]	Tm	Yb [*]	Y	Graphite
Intercept <i>a</i> / mV	186	157	212	182	164	238	215	209	191	275
Tafel slope <i>b</i> / mV	126	114	151	121	120	316	158	184	122	182
<i>j</i> ⁰ /(10 ² A•cm ⁻²)	3.35	4.20	3.94	3.13	4.30	17.6	4.34	7.31	2.72	3.08
Current density range /(A•cm ⁻²)	0.15 ~ 0.6	0.1 ~ 0.7	0.05 ~ 0.7	0.1 ~ 0.6	0.05 ~ 0.35	0.2 ~ 0.7	0.05 ~ 0.35	0.075 ~ 0.7	0.2 ~ 0.4	0.05 ~ 0.7

Σ RE mixed oxide displayed better electrocatalytic activity on CER than simple RE oxide, with the overpotential reducing to 110 mV. Correspondent Tafel slope and exchange current density was 133 mV and 9.17×10^{-2} A/cm² respectively. Good electrocatalytic activity attributes to the properties of RuO₂. The composition and texture of Ru oxide are sensitive to thermal decomposition temperature, and its activity degrade with decomposition temperature lifted. In contrast with RuO₂, thermal decomposition temperature of RE oxide is relative high. Profitable synergistic effect may be obtained when mixing two kinds compounds.

3.3 Mechanism of CER on RE oxide electrodes

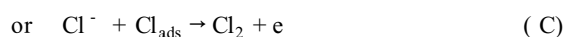
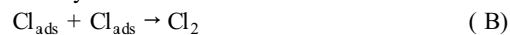
The total reaction of chlorine evolution can be written as



It is generally agreed that the reaction consists of simple reaction steps:



followed by either



Therefore, two possible mechanisms, (A) + (B) or (A) + (C) can be proposed.

Rate equation for reaction steps depends on what adsorption condition (Langmuir isotherm or Temkin isotherm) the absorbed intermediates

Cl_{ads} obey. According to assumed rate-determining step (RDS) and adsorption condition different rate equations can be formulated. Relative theory Tafel slopes deduced from kinetic analysis were listed in Table 3. Experimental Tafel slopes of Pr, Tb, La, Sm, Y, Nd, Tm oxide ranged from 114 to 158 mV, approaching to a slope of 129 mV. Consequently, possible mechanism for CER may be that electrochemical desorption reaction ($\text{Cl}_{\text{ads}} + \text{Cl}^- \rightarrow \text{Cl}_2 + \text{e}$) is the rate-determining step and the adsorption of intermediate species Cl_{ads} obeys non-activated Temkin condition or Langmuir ($\theta \rightarrow 0$) condition.

Table 3 Theoretical slopes from kinetic analysis

Mechanism	Reaction A + C			
$\text{Cl}_{\text{ads}} + \text{Cl}^- \rightarrow \text{Cl}_2 + \text{e}$ (RDS)	Langmuir $\theta \rightarrow 0$	Langmuir $\theta \rightarrow 1$	No activated Temkin	Activated Temkin
$\beta = 0.5$	129	386	129	193

Kinetic studies have mostly been based on Tafel slopes only. However, different mechanism and rate equation often give rise to same Tafel slope. Moreover, many factors affect Cl₂ evolution at oxide electrodes^[11]. In any case it is insufficient to determine reaction mechanism from sole Tafel slope. Therefore, additional diagnostic evidences, such as surficial coverage fraction θ , are always necessary to highlight the

mechanism. Electrochemical chronocoulometric measuring, on RE oxides, as shown in Fig. 4 for Tb oxide, revealed the presence of both adsorbed Cl atom and Cl^- ion on the surface of oxide electrode, which ruled out the mechanism that Cl_{ads} obeys Langmuir isotherm of $\theta \rightarrow 0$. The results of the present study suggested that classic ion + atom route be probable mechanism for the reduction of chlorine on RE oxide electrodes, with the adsorption of intermediate species Cl_{ads} obeying the non-activated Temkin condition.

Fig. 4 $Q-t^{1/2}$ response to double potential step on Tb oxide

Modification in Tafel slope implies that the mechanism of CER has been changed. The reason may be that the adsorption of intermediate on oxide alters the surficial energy state, which makes adsorption noticeable, but no monomolecular layer coverage, so as to accelerate the rate of CER and reduce the overpotential.

4 CONCLUSIONS

(1) Pr_6O_{11} , Tb_4O_7 , Tm_2O_3 and $\Sigma\text{RE} + \text{Ru}$ mixed oxide electrodes showed good electrocatalytic activities on CER, reducing anodic overpotential up to 80 ~ 110 mV at a current density of 0.6 A/cm^2 compared with graphite electrode. Calculated Tafel slopes were 114, 120, 158 and 133 mV respectively. Correspondent exchange current density were 0.042, 0.043, 0.043 4 and 0.0917 A/cm^2 .

(2) The electrocatalytic activity series of RE oxides according to their anodic overpotential reducing was $\text{Pr} \geq \text{Tb} > \text{Tm} > \text{Dy} \geq \text{La} \geq \text{Y} \geq \text{Sm} > \text{Yb} \geq \text{Nd}$.

(3) Transition metal oxides and most of mixed oxides showed no obvious activity on CER under present preparing procedure. Only $\text{Co}_{0.75}\text{Fe}_{2.25}\text{O}_4$ demonstrated some extent electrocatalytic activity with the overpotential reducing up to 80 mV. Correspondent Tafel slope and exchange current density was 137 mV and 0.041 A/cm^2 respectively.

(4) Kinetic analysis on Tafel relationship derived that possible mechanism for chlorine evolution on RE oxide electrode was Heyrovsky reaction ($\text{Cl}_{\text{ads}} + \text{Cl}^- \rightarrow \text{Cl}_2 + \text{e}$) being the rate-determining step, and the adsorption of intermediate species Cl_{ads} obeying the non-activated Temkin condition.

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(Edited by Yuan Saiqian)