# On the development of metallic inert anode for molten $CaCl_2$–CaO System

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## ARTICLE INFO

## ABSTRACT

Some fundamental aspects related to inert anode development in molten $CaCl_2$–CaO were investigated based on thermodynamic analysis, electrochemistry of metals and solubility of oxide measurements. The Gibbs free energy change of several key anodic reactions including electro-stripping of metals, electro-formation of metallic oxides, electro-dissolution of metallic oxides as well as oxygen and chlorine evolution was calculated and documented, for the first time, as a reference to develop metallic inert anode in chloride based melts. The anodic behaviors of typical metals (Ni, Fe, Co, Mo, Cu, Ag, and Pt) in the melt were investigated. The results confirmed the thermodynamic stability order of metals in the melts and revealed that surface oxide formation can increase the stability of the electrodes in CaO containing melt. Furthermore, solubility of several oxides (NiO, $Fe_2O_3$, $Cr_2O_3$, $Co_3O_4$, $NiFe_2O_4$) in pure $CaCl_2$ or $CaCl_2$–CaO melts was measured to evaluate the stability of oxide coating or a cermet inert anode in the melt. It was found that the solubility of NiO decreased with increasing CaO concentration, while that of $Fe_2O_3$ increased. Ni coated with NiO film had much higher stability during anodic polarization.

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## 1. Introduction

Due to its high solubility for oxygen anion, molten $CaCl_2$ and $BaCl_2$ were used as electrolyte for deoxygenation of liquid metals several decades ago, and is becoming a more significant electrolyte for novel electro-metallurgical processes in the very recent decade [1–3]. Both of the so-called FFC process (direct electrochemical reduction of solid oxides) [1] and the OS process [2] (indirect electrochemical reduction of solid oxides) use $CaCl_2$–CaO as electrolyte. The processes, especially the former one, have been successfully demonstrated to produce refractory metals and alloys in a more energy efficiency way [3]. However, cutting $CO_2$ emission is still on the way since a cost-affordable inert anode is still absent in the melt. What is worse, the carbon anode will produce some toxic gases such as dioxin in the melt along with $CO_2$. Furthermore, carbon contamination was found in the cathode product and electrolyte coming from carbon anode erosion and/or the cathodic reduction of anode products ($CO_2$ and/or $CO_3^{2-}$ which transport to cathode through atmosphere and/or electrolyte). An inert anode is crucial for improving the processes in all aspects of environmental protection, energy efficiency and economy. There are several materials including Pt, $SnO_2$, $CaRuO_3$ and alloys reported as inert anode in molten $CaCl_2$–CaO melt [4–7], but a comprehensive consideration of inert anode for the system is still absent.

The attempt to develop an inert anode for the Hall–Héroult process has lasted more than a century [8,9]. Metals/alloys, ceramics, and cermets are mostly investigated materials and plenty of fundamental and practical database have been constructed [10–12]. This provides precious experience and reference for the inert anode development in molten $CaCl_2$–CaO. According to an evolution report issued by the Technical Working Group of ASME sponsored by DOE in 1999, metals were ranked as the first likelihood materials for inert anode among the three kinds of candidate materials. Metals, alloys and metallic based materials are potential promising candidates of inert anode for their high electronic conductivity, excellent thermal shock resistance and mechanical robustness [13,14]. The metallic anode might work stably and effectively with a protective layer, normally oxide layer that was *in situ* or *ex situ* formed.

Comparing with the Hall–Héroult process, the temperature of chloride melts in the FFC process and the OS process is about 100 °C lower and it can be much lower when mixing melts are applied. Moreover, the solubility of oxides in molten fluoride is generally much higher than that in molten chloride, suggesting that oxides might be more stable in molten chloride. For above reasons, developing a metallic inert anode in chloride melts seems to stand more opportunity than in fluoride melts. However, a fundamental database of the stability of metals and oxides in molten $CaCl_2$–CaO is unavailable so far.

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Typical anodic reactions on a metallic anode in molten $CaCl_2$–CaO electrolyte are as follows:
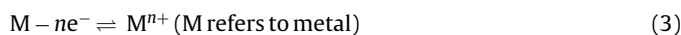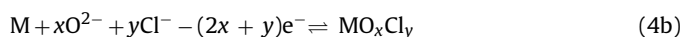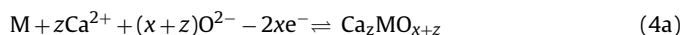
Oxygen evolution reaction (OER):

$$2O^{2-} - 4e^- \rightleftharpoons O_2(g) \tag{1}$$

Chlorine evolution reaction (CER):

$$2Cl^- - 2e^- \rightleftharpoons Cl_2(g) \tag{2}$$

Metal dissolution reaction (MDR):

$$M - ne^- \rightleftharpoons M^{n+} \text{ (M refers to metal)} \tag{3}$$

Metal oxide/compound formation reaction (MOFR) in the presence of oxygen anion:

$$M + xO^{2-} - 2xe^- \rightleftharpoons MO_x \tag{4}$$

or

$$M + zCa^{2+} + (x+z)O^{2-} - 2xe^- \rightleftharpoons Ca_zMO_{x+z} \tag{4a}$$

$$M + xO^{2-} + yCl^- - (2x+y)e^- \rightleftharpoons MO_xCl_y \tag{4b}$$

Metal oxide electrochemical dissolution reaction (MOEDR):

$$MO_x - 2xe^- \rightleftharpoons M^{2x+} + 0.5xO_2(g) \tag{5}$$
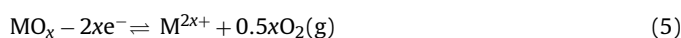
On another aspect, the metal oxides formed through reaction (4) might dissolve in the melt through metal oxide chemical dissolution reaction (MOCDR):

$$MO_x + xCaCl_2 \rightleftharpoons MCl_{2x} + xCaO \tag{6a}$$

$$MO_x + xCl_2(g) \rightleftharpoons MCl_{2x} + 0.5xO_2(g) \tag{6b}$$
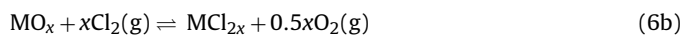
OER (reaction (1)) is the desirable reaction on an inert anode, which produces non-toxic oxygen as by-product. However, toxic chlorine gas might be generated through reaction (2) (CER). The potential of OER is ~0.58 V more negative than that of CER at the unit activity of oxygen and chloride ion so that thermodynamically the OER will prefer to CER during anodic polarization even taking the difference of anion activity into account. The ideal anode working potential should be kept in the potential range between OER and CER so that only oxygen evolution reaction takes place on the anode. When a metallic material is selected as a candidate of inert anode, it might work in one of the following conditions:

(1) The metal itself is stable enough under anodic polarization until chlorine evolution, i.e., the equilibrium potential for MDR (reaction (3)) is nobler than that of CER, at least nobler than that of OER.
(2) The metal is covered by an electronic conductive and protective film which is *in situ* formed through MOFR (reaction (4)) or *ex situ* formed by oxidation or coating. As an immediate requirement, the film should neither dissolve into the melt at the working condition in a chemical way (reaction (6)) nor in an electrochemical way (reaction (5)).

The aim of current research is to investigate the possibility of metallic materials as inert anode in molten $CaCl_2$–CaO theoretically and experimentally. In this paper, the thermodynamic data of metals related to the above anodic reactions are calculated using the data from HSC Chemistry [15] in molten $CaCl_2$–CaO, and then the anodic polarization curves of some typical metals are measured to verify the calculation. The impacts of oxygen anion in the melts on the stability of metallic electrodes are also investigated. Furthermore, the solubility of some oxides in molten $CaCl_2$ is studied to evaluate the stability of the surface oxide layers. Finally, the concept of oxide coating metallic electrode is demonstrated.

## 2. Experimental

### 2.1. Anodic polarization curve measurement

An alumina crucible (30 mm × 200 mm) containing 40 g anhydrous $CaCl_2$ (analytical purity, Sinopharm Chemical Regent Co. Ltd., China) or $CaCl_2$–NaCl (in 1:1 molar ratio) or them with certain amount of CaO (≥99.99%, Sinopharm Chemical Regent Co. Ltd., China) was put into a sealed close-one-end quartz tube reactor. The reactor was slowly heated to 350 °C in 5 h and kept at 350 °C for at least 24 h to remove residual moisture and then the temperature was raised and kept at 1123 K (850 °C) for $CaCl_2$ melt or 1023 K (750 °C) for $CaCl_2$–NaCl melt at a rate of 100 °C per hour in argon (≥99.999%) atmosphere following the literatures [16,17]. And then pre-electrolysis was applied between a Mo wire and a graphite electrode under a cell voltage of 2.7 V linked with a cell testing system (Shenzhen Neware Electronic Co. Ltd., China) for 2 h. Metallic wires (d = 1 mm, Alfa Aesar) and a graphite rod (d = 5 mm, analytical purity) connected with a molybdenum wire (d = 2 mm) was served as working electrode and counter electrode, respectively. A platinum wire (d = 0.5 mm, 99.5%) was used as pseudo-reference electrode, its potential was checked periodically and calibrated by the $Ca^{2+}$/Ca potential using a Mo wire electrode. All of the electrode potentials are reported with respect to the $Ca^{2+}$/Ca potential. The electrochemical measurements were operated and recorded on a CHI660B electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China) linked to a PC computer. A NiO coated nickel wire was also used as working electrode to test the effect of NiO coating on the anodic behavior. The oxide layer was prepared by simply sintering Ni wire in air at 900 °C for 2 h. The morphology of the obtained oxide layer was characterized by SEM (FEI Sirion field emission gun).

### 2.2. Solubility test of oxides

NiO, $Fe_2O_3$, $Co_3O_4$, $Cr_2O_3$ (AR grade purity) were purchased from Sinopharm Chemical Regent Co., Ltd. and fully dried in an oven before testing. $NiFe_2O_4$ was synthesized from NiO and $Fe_2O_3$ mixed oxides through sintering at 1250 °C for 2 h [18,19] and its composition was confirmed by X-ray diffraction spectrometry (XRD, SHIMADZU X-ray 6000 with Cu-Kα). 300 g anhydrous $CaCl_2$ was put into an alumina (99%, 80 mm × 150 mm) crucible which was sealed in a stainless steel reactor. The anhydrous $CaCl_2$ was carefully dried following aforementioned drying and temperature raising process so that the hydrolysis of $CaCl_2$ was neglectable. The reactor was protected by continuous argon flow. About 2.0 g oxide powder was put into the melts under stirring with an alumina rod. It should be pointed out here that although thermodynamically $Al_2O_3$ could dissolve and/or react with the melt and other oxides, it was found the sintered dense alumina crucible and rod was kinetically stable. There was no observable change with the alumina crucible and rod after long time test and the alumina crucible was also reported as container of the melt by others [20–22]. In some tests, certain amount of CaO was added into the melt to evaluate the effect of CaO on the solubility. Some amount of liquid melt was sampled from the container using a small alumina crucible (13 mm × 15 mm) at different time during the solubility test at high temperature. The small crucible with sampled melt was weighed in hot very quickly and put into a small beaker which contained 20 mL $HNO_3$ (3 mol L$^{-1}$) and the beaker was boiled about 10 min in order to promote thoroughly dissolving of oxides and lower the concentration of $HNO_3$. Then the solution was transferred into a 100 mL standard vessel flask. The metallic ion concentration was analyzed by Atomic Adsorption Spectroscopy (AAS, PerkinElmer Inc., Aanalyst 800). The solubility of oxide was then calculated from the analysis results by following