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A new anode material for oxygen evolution in molten oxide electrolysis

Antoine Allanore¹, Lan Yin^{1,♦}, and Donald R. Sadoway¹

The development of a stable anode material for chlorine evolution in the 1960s by H. Beer and the de Nora brothers is arguably the last technological breakthrough in industrial electrolysis¹. To practice the principles of green chemistry, extractive metallurgy awaits a discovery of comparable magnitude directed at the mitigation of greenhouse gas emissions. This quest was initiated for aluminium extraction by C. M. Hall in the 1890s². Molten oxide electrolysis (MOE) is an electrometallurgical technique that enables the direct production of metal in the liquid state from oxide feedstock^{3,4}, offering both a drastic simplification of the process flow-sheet and a significant reduction in energy consumption⁵. MOE is considered a promising route for mitigation of CO₂ emissions in steelmaking^{5,6,7}, production of metals free of carbon⁸, and generation of oxygen for extra-terrestrial exploration^{9,10}. To date, MOE has been demonstrated using anode materials that are consumable (graphite for ferro-alloys and for titanium^{8,11}) or unaffordable for terrestrial applications (iridium for iron^{12,13}). To enable metal production without process carbon, MOE requires an anode material that resists depletion while sustaining oxygen evolution. The challenges for iron production are threefold. First, the process temperature is in excess of 1538°C¹². Secondly, under anodic polarization most metals inevitably corrode in such highly aggressive media^{13,14,15}. Thirdly, iron oxide is subject to spontaneous reduction upon contact with most refractory metals¹⁶ and even carbon.

Herein we show that anodes comprising Cr-based alloys exhibit limited consumption during iron extraction and oxygen evolution by MOE. The anode stability is due to the formation of an electronically conductive solid solution of chromium (+III) and aluminium oxides in the corundum structure. These findings now make practicable larger-scale evaluation of MOE for the production of steel and provide a key material component necessary to ultimately offer mitigation of greenhouse gas emissions while producing metal of superior metallurgical quality.

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1 Cr-Fe_x alloys have been tested as bulk anode materials under electrochemical conditions
2 previously demonstrated as successful for iron extraction¹². The mass fraction of iron in the alloy (x)
3 has been varied between 0 and 30%, the iron-rich limit corresponding to an alloy melting point equal
4 to the process temperature (1600°C). The selected electrolyte composition is very basic (optical
5 basicity of 0.75), which is advantageous for its physico-chemical properties, e.g., electrical
6 conductivity and viscosity, but challenging in terms of anode materials compatibility¹³.

7 The electrolysis cell operated in constant current mode (Fig. 1a) at an average anode current
8 density exceeding 2 A.cm⁻² exhibits a low cell voltage, which reached a steady value of around 3.8 V
9 after slightly less than 2 h. Increasing the current density does not lead to an intolerable increase in
10 the cell voltage, although there is an increase in its amplitude of variation. Observation of the
11 electrolyte surface close to the anode during electrolysis confirms the evolution of gas
12 (**supplementary movie**), the generation and accumulation of which in such a small cell has a
13 noticeable impact on the voltage variation with time. The fact that the oxygen content of the outlet
14 gas gradually reaches values comparable to those observed with a noble-metal anode in the same
15 cell¹³ is evidence of successful production of oxygen with this new anode material. Its measured
16 faradaic efficiency based on the recovered oxygen and taking into account typical consumption by
17 oxidation of the inactive parts of the furnace (molybdenum current collectors mainly) is around
18 24%, similar to that previously obtained with an iridium anode. Furthermore, the oxygen
19 concentration in the anode off-gas scales with current density. The simultaneous production of metal
20 is confirmed by the observation of the cathode after electrolysis (Fig 1b). The iron metal, which has
21 alloyed with the molybdenum cathode substrate, contains almost no carbon (<25 ppm), a small
22 amount of chromium (<500 ppm), and an amount of oxygen in agreement with that predicted by
23 thermodynamics for carbon-free iron at 1600°C (<4000 ppm). At the cathode the corresponding
24 faradaic efficiency is 34%, in close agreement with previous investigations^{12,13}. Along with these
25 promising electrochemical results, the anode stability has been demonstrated (Fig1c): the external
26 dimensions have barely been affected by electrolysis, as confirmed by repeated testing for various
27 durations with a plurality of alloy compositions (**supplementary Figure S1**). The anode shows
28 coverage by electrolyte (so-called drag-out) that has adhered to the surface.

29 The efficiency and stability of the Cr-Fe alloys for oxygen evolution is in agreement with
30 thermodynamic calculations, which predict the solid chromium oxidation product to be stable in
31 molten electrolyte (**supplementary discussion A, Figure SA2**). However, a study of the anode
32 microstructure after electrolysis (Fig. 2a & **supplementary Figure S2**) suggests a more sophisticated

1 mechanism. First, limited internal oxidation of the alloy is observed together with chromium
2 depletion in the bulk metal of $\sim 10\%$, effective over a distance of approximately $150\ \mu\text{m}$ (Fig. 2b).
3 Secondly, and of relevance to overall anode stability, a triplex scale is observed at the alloy surface:
4 metal oxide/mixed oxide/frozen electrolyte. EDS analysis (Fig. 2a) and optical observations under
5 polarized light (Fig. 2c) reveal that the oxidation products are found in two layers: an inner layer of
6 chromium oxide (Cr_2O_3) containing few percent of aluminium, and an outer layer composed of a
7 solid solution of Cr_2O_3 and Al_2O_3 .

8 The crystallographic structures of these phases have been confirmed by XRD analysis of the
9 inner side of the crust (Fig. 2d, targeting from the alloy side) and the powder obtained by crushing
10 the entire crust (Fig. 2e). In this latter case, a signal from the frozen slag is also noticeable. A small
11 amount of chromium has been found in the electrolyte close to the anode (Fig. 2a), in agreement
12 with both the thermodynamic prediction and the experimental measurements of chromium oxide
13 chemical solubility in an oxide melt of this specific composition (**supplementary discussion A**).
14 The composition and morphology of the oxide scale was found to be pretty much independent of
15 the composition of the base alloy, which influenced mainly the extent of chromium depletion
16 (**supplementary Figure S2**). In the case of pure chromium, the inner layer proved to contain a
17 higher concentration of aluminium, and the outer layer exhibited a non-negligible concentration of
18 calcium.

19 The influence of electrolysis duration on the thickness of the chromium (+III) oxide
20 containing layer did not prove to be significant (for CrFe_{10} : $75\pm 16\ \mu\text{m}$ after 2.5h as compared to
21 $42\pm 38\ \mu\text{m}$ after 5.2h) on the time-scale investigated, which was limited by the crucible material
22 performance. In contrast, the initial concentration of iron in the anode was found to be of major
23 importance: an anode containing 30% iron in the starting material proved to develop thicker
24 chromium oxide containing layers (for CrFe_{30} : $115\pm 26\ \mu\text{m}$) and to incur higher internal depletion
25 of chromium, leading to the formation of a low melting point alloy responsible for faster local
26 consumption and anode re-shaping alloy fusion (**supplementary Figure S1 and S2**).

27 Dry oxidation studies conducted on the same alloys in similar conditions proved that the rate
28 of chromium oxide formation during electrolysis was comparable ($36\pm 16\ \mu\text{m}$ after 2.5h) and not
29 sensitive to either the oxygen concentration or the alloy iron content (**supplementary discussion**
30 **B, Figure SB2 and SB3**), suggesting that electrolysis did not lead to an inescapable increase in the
31 oxidation rate of the metal. The application of existing oxidation theory (**supplementary**

1 **discussion B, Figure SB5**) suggests that in this specific electrolysis case external polarization
2 creates an electric field of such small magnitude across the anode scale as to have almost no
3 influence on the oxide growth rate.

4 Chromium alloys immersed in the molten electrolyte in the absence of electrolysis (Fig. 3a)
5 proved to develop a thicker layer ($98\pm 29\ \mu\text{m}$ of chromium rich oxide layer after 5h) than in either
6 the electrolysis or the dry oxidation cases. Analysis of the chromium rich oxide layers also reveals the
7 presence of a calcium spinel phase containing chromium and aluminium (Fig 3a and **supplementary**
8 **discussion A, Figure SA4**).

9 The results obtained under electrolysis show that the oxide scale formed on the alloy is
10 principally a solid solution of chromium oxide (+III) and alumina, whereas without polarization a
11 calcium spinel phase predominates. The phase diagram for alumina-chromium (+III) oxide-calcia
12 (Fig. 3b) confirms that at low calcia concentration, in green on the diagram, the stable chromium-
13 containing solid-oxide phase is indeed the solid solution with alumina. It is likely that electro-
14 migration under the influence of electrolysis is responsible for driving away the positive calcium ions
15 (calcium ion is the dominant cation in the electrolyte, while aluminium is present as an aluminate
16 anion) leading to the formation of a calcium-free solid solution of chromium and aluminium on the
17 anode. From an oxidation perspective, the formation of the solid solution in place of the calcium
18 spinel is seen as beneficial since chromium diffusivity is expected to be smaller in the corundum
19 structure than in the spinel. The diffusivity of Cr^{3+} in the chromia-alumina solid solution is also
20 predicted to be smaller than in a pure chromium oxide phase owing to the difference in lattice
21 constant¹⁷. Finally, the formation of such a solid solution may also modify the rate-determining step
22 for oxidation, since it has been shown that the oxygen coverage on such material is much poorer
23 than in the case on pure chromium (+III) oxide¹⁸.

24 These results have two-fold consequences. First, the successful extraction of metal and
25 oxygen obtained with an affordable alloy-based anode material at the bench-scale will enable the
26 design of a reactor of sufficiently large scale that longer term MOE performance can be properly
27 assessed, e.g., specific energy consumption and cell service lifetime. This is especially important in
28 light of the fact that the values of such performance characteristics obtained in the present
29 laboratory scale cell configuration are not considered as representative of industrial conditions. The
30 same disparity holds for other high-temperature electrolytic technologies, notably the Hall-Héroult
31 process for extraction of aluminium¹⁹. Encouraging signs are to be found in the results of previous
32 large-scale production of manganese by MOE⁸. Secondly, the oxidation behavior of alloys in such

1 an extreme environment has resulted in a novel configuration, i.e., the formation of an oxide solid
2 solution containing one element not present in the base alloy, that challenges high-temperature
3 oxidation theory. Further work will involve the application of existing passivation theory, e.g., Point
4 Defect Model²⁰, to the specific case of molten oxide electrolytes.

5

Methods summary

The original set-up described elsewhere¹³ has been adapted for the investigation of a non-noble metal anode as presented in the Methods Section. In summary, a vertical tube furnace constantly purged with helium is used to maintain the cell temperature. The process outlet gas composition is monitored with a gas chromatograph, which measured an average O₂ content before electrolysis of around 50 ppm. The cell consists in an yttria-stabilized zirconia crucible containing the oxide mixture (in wt%: 42.3 CaO, 42.3 Al₂O₃, 5.4 MgO and 10 Fe₃O₄), pre-melted prior to the electrolysis experiment. All electrodes are immersed into the electrolyte from the top of the furnace, through a gas-tight cap equipped with vacuum-type feedthroughs. The horizontal cathode consists of two molybdenum disks, 3.8 cm in diameter and 0.1 cm thick, attached by nuts of the same material to a threaded molybdenum lead, 0.5 cm in diameter.

The Cr-Fe alloys were prepared by arc melting high purity metals (min. 99.95%) of known weight. Anode shapes were cut to dimensions (typically 2 × 1 × 0.7 cm) by water-jet. The anode surfaces were ground by belt sander with #220 grit SiC paper prior to welding. Samples were connected to molybdenum leads, 0.3 cm in diameter and 90 cm long, by tungsten inert gas welding in a box flushed with argon.

Evaluation of the dry oxidation features of the alloys under investigation has been conducted using a thermogravimetric analyzer and vertical tube furnace.

Details on observation and characterization methods are provided in the Methods Section.

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The following Supplementary Information is available online:

Supplementary movie (*Visualisation of oxygen evolution, filename 'Allanore_Anode_Suppmovie.mp4'*),
Supplementary Figure S1 (*Optical macrographs of the anodes after electrolysis, for various alloy compositions*) and
S2 (*Cross-sectional optical micrographs of the anode / electrolyte interface after electrolysis,
for various alloy compositions*), Supplementary data and discussion A (*Chemical stability of chromium oxide
(+III) in calcia-rich electrolyte containing iron oxide*) and B (*Chromium and chromium-iron alloys oxidation kinetics
at high temperature*).

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Authors Contributions

A.A. conceived the idea and designed the study based on principles enunciated by D.S. A.A. and Y.L. performed the experiments, the analysis of the results, and wrote the original draft of the paper. D.S. edited the original manuscript and revised it for submission. All authors discussed the results and commented on the paper.

Author Information

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Methods Section

Electrolysis experiments.

The electrolyte chosen for electrolysis was composed of multiple oxides (CaO, MgO, Al₂O₃), in which 10 wt% of magnetite (Fe₃O₄) was added as iron oxide feedstock. The composition and properties of the electrolyte have been provided in [13]. The high concentration of ionic compounds - calcia mainly - is responsible for some important features of this electrolyte for electrolysis, e.g. (i) high electrical conductivity; (ii) low melting point; (iii) low density and viscosity. The oxide powders were purchased from laboratory chemicals suppliers, with purity higher than 99 wt%. These powders were mixed in polyethylene bottle and pre-melted in sacrificial magnesia crucibles to reduce experimental artifacts. This step had been identified as crucial for successful anode stability: if not removed prior to the electrolysis test, impurities entrapped in the oxide compounds, such as water vapor were released during furnace ramping and lead to contamination of the anode surface, leading to poor performance during electrolysis.

Yttria-stabilized zirconia crucibles (5wt% Y₂O₃, 6.6 cm diameter, 10.5 cm height, Jiangsu Province Ceramic, China) were used as the electrolyte container. A high purity magnesia crucible (99.8 wt%, Ozark Technical Ceramics, USA) was used as a secondary container to protect the tube furnace in case of failure of the inner zirconia crucible.

Chromium alloyed with x wt% iron (CrFe _{x} alloy, x ranging from 0-30 wt%), has been assessed for its suitability as an oxygen evolving anode. Strips of 1 cm thickness of these alloys were provided by Ames lab, obtained by arc melting in argon atmosphere and were cut into coupons by water jet to typically $2.0 \times 1.0 \times 0.7$ cm with a top-pin of around $1.0 \times 0.5 \times 0.7$ cm for welding. The surface of the anode was polished with #220 SiC papers. The pin of the anode was welded to a molybdenum rod (0.3 cm diameter, 90 cm height, American Elements, USA) that served as a current lead. Two molybdenum disks of 0.1 cm thickness and 3.8 cm diameter served as the cathode. These disks were connected to a threaded molybdenum rod by molybdenum nuts. Molybdenum leads were protected by high-purity alumina tubes, and high purity alumina paste (Resbond 989, Cotronics Corp., USA) was used to protect connections in the head space above the electrolyte. The immersed part of the cathode lead was protected with an extra magnesia or zirconia tube. The anode was held vertically above the horizontal cathode disk, the corresponding projected anode area on the cathode being typically 1.4 cm^2 . This value was used in the estimation of anodic current densities.

The high-temperature pre-oxidation of the anode alloys as well as the electrolysis experiments were conducted in a vertical tube furnace fitted with lanthanum chromite heating elements (Model:

PVT 18/100/350 with 3216P1 controller, Carbolite, UK) and a closed-one-end alumina tube (11.4 cm inner diameter, 1 m height, 99.8%, McDanel Advanced Ceramics, USA).

The crucible containing solid pre-melted electrolyte was placed in the hot-zone of the furnace tube, the two electrodes suspended above the crucible contents during ramping of the temperature.

High purity helium was continuously flowed through the tube furnace at a flow rate of $250 \text{ Ncm}^3 \cdot \text{min}^{-1}$ to maintain an inert atmosphere. The oxygen content of the process outlet gas was analyzed by gas chromatography (CP-4900 Micro-Gas Chromatograph, Varian Inc., USA) and was measured to contain less than 50 ppm oxygen during furnace temperature ramping and prior to electrolysis. The continuous monitoring of the oxygen level and the gas flow-rate at the reactor outlet allow to estimate the anodic faradaic efficiency specific to this laboratory configuration. One has to be however aware of the limitation of this method since part the oxygen is consumed by the oxidation of the metallic parts present into the tube furnace, in particular by the molybdenum current collectors. A control experiment was conducted in which a known quantity of oxygen was flushed at the inlet (1% O_2 in He at $300 \text{ Ncm}^3 \cdot \text{min}^{-1}$). The corresponding oxygen level at the reactor outlet (0.5%) suggested that around $\frac{1}{2}$ of the oxygen could be consumed by internal oxidation. This 50% loss in measuring the oxygen outlet concentration has been taken into account in the anodic faradaic efficiency estimates reported in the main text. The cathode efficiency has been estimated by chemical titration (ICP-OES) of the iron content of $\frac{1}{4}$ of the molybdenum disc cathode after electrolysis. The first set point of the furnace was 1450°C with a ramping rate of $1.5^\circ\text{C}/\text{min}$, followed by dwelling for 2 h. This first step allowed pre-oxidation of the anode and the formation of a protective chromium (III) oxide layer on the anode surface. The second set point was 1600°C , the temperature at which the cathode was immersed 3 cm into the electrolyte. The anode was lowered afterwards under anodic polarization (constant voltage of 2 V) by 1 cm. A type-B thermocouple was also positioned above the molten electrolyte level to monitor the process temperature: 1565°C for a furnace set point of 1600°C . Galvanostatic electrolysis (Argantix XDS30-500-208IF, California Instruments Corp., USA) was conducted at currents ranging from 2A to 9A for a duration ranging between 1.5 and 6 hours. After electrolysis, both electrodes were raised out of the melt to a relatively cold zone in the furnace to preserve the reaction products.

Dry oxidation experiments.

Oxidation experiments were carried out both in a thermogravimetric (TG) analyzer (NETZSCH STA 409) and the vertical tube furnace. The TG samples were CrFe_x alloy beads of around 200 mg

produced by arc-melting in argon atmosphere. Oxidation of CrFe_x ($x=10, 20$ and 30) alloys at 1600°C in Ar for 3 hours was investigated in the tube furnace, emulating the electrolysis process. Each sample was submitted to the same preparation and experimental procedure as that for electrolysis.

Chromium oxide (III) stability experiments

The CrFe_{10} alloy (same as that for electrolysis) and sintered Cr_2O_3 pellets were used to study the stability of Cr_2O_3 in molten electrolyte at 1600°C in the absence of polarization using the vertical tube furnace.

Post-experiments observations and analysis

The samples were disassembled for detailed characterization at room temperature. Part of the crust on the alloy surface was peeled off for scanning electron microscopy - energy dispersive X-ray spectroscopy (SEM-EDS, Leo VP438) analysis on both inner and outer surfaces. Various phases on the inner surface, outer surface, and in the bulk of the crust after crushing to powder were identified by x-ray diffraction (X'Pert Pro Multipurpose Diffractometer, PANalytical, Netherlands). Cross-sections were obtained by mounting in thermosetting polymer, cutting with a diamond saw, and polishing with SiC papers and diamond solution down to $1\ \mu\text{m}$. A high magnification optical microscope (Olympus GX51) and SEM were used to investigate the cross-sectional surface. The carbon content of the iron product on the cathode was measured by Leco combustion technique. Direct current plasma coupled with atomic emission spectroscopy was used to analyze the iron, chromium and molybdenum contents of the cathode deposit.

Statistics

Oxide layer thicknesses in the text are given as (mean \pm standard deviation) based on measurements at 10 locations along the layer.





