



Direct electroreduction of oxides in molten fluoride salts

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ABSTRACT

A new kind of electrolyte composed of molten fluorides has been evaluated in order to perform a feasibility study of the direct electroreduction reaction. The direct reduction of SnO₂ and Fe₃O₄ was realised in LiF–NaF at 750 °C and in LiF–CaF₂ at 850 °C for TiO₂ and TiO. The electrochemical behaviour of these oxides was studied by linear sweep voltammetry: a current corresponding to the oxide reduction was evidenced for TiO₂, SnO₂ and Fe₃O₄. After galvanostatic electrolyses, a complete conversion was obtained for all oxides, except TiO, and the structure of reduced Ti and Fe samples had a typical coral-like structure while dense drops of Sn were recovered (Sn is liquid at operating temperature). After TiO electrolysis, a thin external metallic titanium layer was detected, acting as a barrier for the oxide ion diffusion and no complete reduction can be achieved. This could be explained by a Pilling–Bedworth ratio around 1 for Ti/TiO.

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1. Introduction

In the last decade, a new electrochemical process has been developed in order to convert solid oxides into their metal: the direct electrochemical reduction. Chen et al. [1] have first achieved the direct reduction of TiO₂ into Ti in a molten chloride salt composed of CaCl₂. This innovative method is now often referred as the FFC (Fray–Farthing–Chen) Cambridge process, where the overall reaction is the oxygen removal from a solid M_xO_y oxide at the cathode (1) and the formation of CO₂(g) at the carbon anode (2), according to:



The FFC process has been intensively studied worldwide, exclusively in molten chloride salts (LiCl or CaCl₂), for different purposes: high purity Si production [2], spent nuclear fuel processing (reduction of rare earth oxides [3], UO₂ [4], U₃O₈ [5], MOX [6], spent fuel [7], etc.), pure metal or alloy production (reduction of Nb₂O₅, Fe₂O₃, NiO–TiO₂, etc. [8–10]). No data are available in the literature for the electrochemical reduction of SnO₂, TiO and Fe₃O₄ whereas TiO₂ has been intensively studied in chloride salts [1,11–13]. In molten CaCl₂, its reduction pathway has been proposed [14] and several titanium sub-oxides have been characterised (Ti₄O₇, Ti₃O₅, Ti₂O₃, CaTi₂O₄).

However, up to now, no process has reached the industrial scale. A recurrent problem is that the final product is often polluted by carbides, due to the reduction of carbonates CO₃²⁻ formed by the reaction of the CO₂(g) anodic product with O²⁻ cations dissolved in the salt [15]. Furthermore, carbon particles coming from the anode often causes shortcuts in the cell. An option to avoid carbide formation is to use an oxygen evolving anode, on which the electrochemical reaction is:



However, this reaction is difficult to control in chloride salts due to the close potentials of Cl₂(g) and O₂(g) evolution [4], and corrosion occurs on anodic materials like Pt [16] or SnO₂ [17].

In this work, a different category of electrolyte was tested, i.e. the molten fluorides, with the advantage of using an inert gold anode, allowing O₂(g) evolution [18] as presented in Fig. 1(a). If the oxide concentration in these molten solvents is high enough, corrosion of such anodic material will not occur.

The direct reduction was applied to four different oxides: SnO₂ and Fe₃O₄ in LiF–NaF at T=750 °C and TiO₂ and TiO in LiF–CaF₂ at T=850 °C, with the main purpose of the first assessment of the feasibility of the reduction reaction.

The first part of the work is dedicated to the electrochemical characterisation of oxide samples by linear sweep voltammetry. Then, galvanostatic electrolyses have been performed on small amounts of oxide pellets (~200–300 mg) and the reaction products have been characterised by SEM-EDX and XRD.

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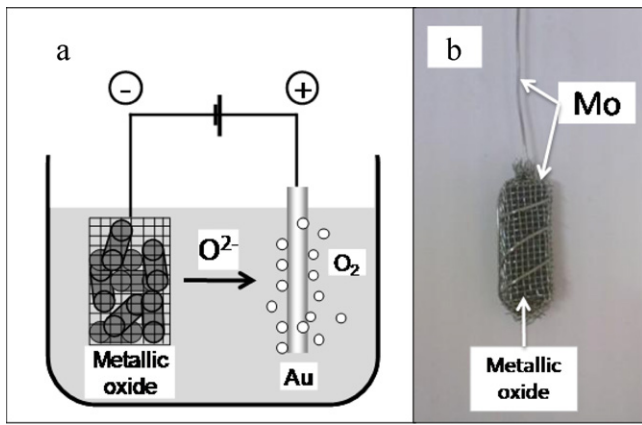


Fig. 1. (a) Schematic representation of the FFC Cambridge process and (b) picture of metallic oxide sample.

2. Experimental

The cell consisted of a vitreous carbon crucible placed in a cylindrical vessel made of refractory steel. The inner part of the walls was protected against fluoride vapours by a graphite liner. Experiments were performed under inert argon (U grade) atmosphere. More details can be found in a previous paper [19].

The electrolyte (200 g) was composed either of the eutectic LiF–CaF₂ (79–21 molar) or of the eutectic LiF–NaF (61–39 molar), from Carlo Erba Reagents (99.99%). The salt mixtures were dehydrated by heating under vacuum ($\sim 10^{-4}$ bar) from room temperature up to the melting point (767 °C and 649 °C respectively) for 72 h. 2 g of lithium oxide (Li₂O) powder (Cerac 99.5%) were added after salt melting to provide oxide ions into the bath. The Li₂O concentration was maintained at a concentration higher than 1 mass.% during electrochemical runs, ensuring that the anodic reaction corresponded to oxygen formation, and thus, preventing the gold oxidation.

TiO₂, TiO, SnO₂ and Fe₃O₄ were used in the form of sintered pellets (Alfa Aesar 99.9%). The oxide pellets, attached with a molybdenum grid connected to the current lead thanks to a molybdenum wire (Fig. 1(b)), were used as working electrodes. The auxiliary electrode was a gold wire with a large surface area ($S = 3.6$ cm²) and all potentials were referred to a platinum wire (0.5 mm diameter), acting as a quasi-reference electrode Pt/PtO_x/O²⁻ [20].

The electrochemical experiments were performed with an Autolab PGSTAT 30 potentiostat/galvanostat. After resin embedding and polishing, the cathode bulk was examined with a scanning electron microscope (LEO 435 VP) equipped with an EDS probe (Oxford INCA 200). XRD characterisations were performed with a Diffractometer D5000 Siemens.

3. Results and discussion

3.1. Solvent selection

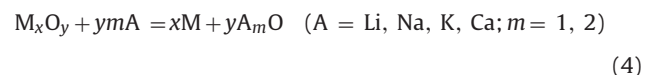
In order to perform the direct electrochemical reduction of a given metal oxide in fluoride mixtures, solvent selection is important: reduction of the metal oxide has to occur at a potential more positive than the alkaline/alkaline earth deposition one. A thermodynamical study has been carried out, using data from [21] and taking into consideration both the solvent components (metal, fluorides and oxides compounds) and the oxide to be reduced. The most common fluoride salts, composed of binary mixtures based on LiF, NaF, KF and CaF₂, have been taken into account.

Table 1

Standard free energy data related to the relative stability of Li, K, Na, Ca (Eq. (5)) and Li₂O, K₂O, Na₂O, CaO (Eq. (6)) in fluoride media (data from [21]).

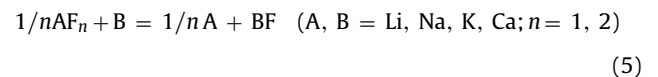
Reaction	Standard free energy $\Delta_r G^\circ$ (J mol ⁻¹) at 800 °C
KF(s) + Li(liq) = K(g) + LiF(s)	-52,892
NaF(s) + Li(liq) = Na(liq) + LiF(s)	-47,464
0.5CaF ₂ (s) + Li(liq) = 0.5Ca(s) + LiF(s)	13,137
K ₂ O(liq) + 2LiF(s) = 2KF(s) + Li ₂ O(s)	-139,381
Na ₂ O(s) + 2LiF(s) = 2NaF(s) + Li ₂ O(s)	-90,582
CaO(s) + 2LiF(s) = CaF ₂ (s) + Li ₂ O(s)	39,935

- (i) The Gibbs energy ($\Delta_r G^\circ$) of the reaction between a metal oxide and an alkaline metal indicates whether the oxide is reduced by the alkaline:



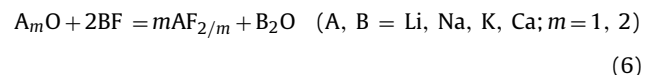
If $\Delta_r G^\circ$ is negative, the oxide reduction occurs at a potential more positive than the solvent alkaline deposition and the direct reduction is then achievable thermodynamically. If $\Delta_r G^\circ$ is positive, an A_mO activity decrease (i.e. a decrease of its concentration in the molten salt) may allow the reduction reaction to occur [22].

- (ii) Since binary fluoride mixtures are considered, the relative stability of alkaline/alkaline earth metal has to be established, in order to determine which A-compound is involved in Eq. (4):



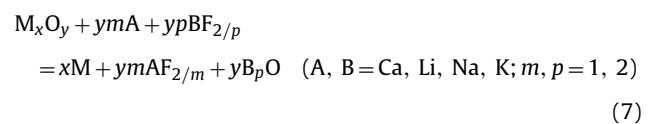
Calculated standard free energy data at 800 °C related to Eq. (5) are compiled in Table 1, considering the LiF/Li redox system as a reference (B=Li in Eq. (5)): the Gibbs energy of reaction (5) is negative for KF and NaF compounds, meaning that they are reduced at a more positive potential than LiF. On the other hand, CaF₂ is reduced at a potential more negative than LiF. The relative stability of the metals, which is valid in the 500–1000 °C temperature range, is thus: Ca < Li < Na < K. As a consequence, in the case of the reduction in LiF–CaF₂ mixtures, the first metal to be formed will be Li, while Na is favored in LiF–NaF mixtures.

- (iii) A last equilibrium to consider in the case of the direct reduction of metal oxides in binary fluoride mixtures is the relative stability of the alkaline oxides produced according to Eq. (4). Indeed the oxide A_mO related to the most stable alkaline is likely to react with the fluoride compound $BF_{2/m}$ of the less stable alkaline according to:



The Gibbs energy of reaction (6), indicated in Table 1 with LiF/Li₂O as a reference (B=Li in Eq. (6)), allows a relative stability of oxides to be established: CaO > Li₂O > Na₂O > K₂O.

- (iv) Combining Eqs. (4) and (6), the overall general reaction to be considered in a binary system is:



As discussed for Eq. (4), if $\Delta_r G^\circ$ of reaction (7) is negative, the metal oxide reduction should occur at a potential more pos-

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