



On the nature of the current and the absence of an *IR*-drop in an FFC-Cambridge-type electro-deoxidation cell



Carsten Schwandt

Department of Materials Science and Metallurgy, University of Nizwa, Birkat Al Mouz, 616, Nizwa, Oman

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ABSTRACT

The fundamental concepts of the FFC-Cambridge-type electro-deoxidation cell for the solid-state conversion of metal oxides to metals are revisited and, based upon these, an expression is presented which describes the transport of oxide ions across the molten salt electrolyte. It is shown that when the amount of the CaO solute in the molten salt electrolyte is negligible with respect to that of the CaCl₂ solvent, the oxide ion transport through the electrolyte is of a diffusional nature and has no migrational component. Under such conditions the electrolyte has no electric field across it and is thus an equipotential volume. The implications of these findings are discussed with regard to the general practicability of an FFC cell and with regard to the soundness of the mathematical models presented hitherto on the ionic transport in FFC cells. It is shown that all models need to be dismissed, because they erroneously endeavour to model the transport of oxide ions by migration rather than by diffusion, and they incorrectly assume the presence of an *IR*-drop across the electrolyte.

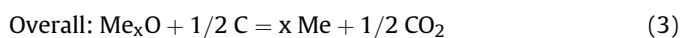
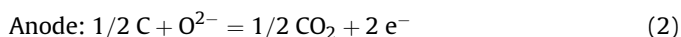
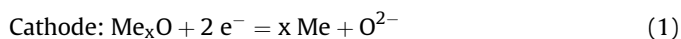
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1. Introduction and fundamentals of the FFC-Cambridge process

The FFC-Cambridge process, named after its inventors and its place of invention, and first published in the open literature in the year 2000 [1], is becoming a recognised metallurgical method for the direct conversion of pure and mixed metal oxides into the corresponding metals and alloys. The fundamental concept of the process is that a solid metal oxide is made the cathode versus a carbon anode in a molten salt electrolyte. The cathodic potential must be chosen such that it is positive enough to preclude electrolysis of the electrolyte, but negative enough to enable ionisation of the oxygen and release in the form of O²⁻ ions. The molten salt electrolyte is typically based on CaCl₂, because it has a high thermodynamic stability and a large solubility for CaO and thus for O²⁻ ions. For pure CaCl₂ at the typical operating temperature of 900 °C the decomposition potential is 3.2 V [2] and the CaO solubility is 20 mol% [3]. The process is sketched in Fig. 1.

The overall electrode reactions and the overall cell reaction of the FFC-Cambridge process read as follows, when carbon is used as

the anode and CO₂ is formed as the off-gas.



The FFC-Cambridge process is a generic technique suitable for the reduction of numerous pure and mixed metal oxides. Its versatility in terms of oxide starting materials and metallic products has been highlighted in recent review articles [4–6]. Significant progress towards commercialisation has also been reported [7,8]. While the FFC process is conceptually straightforward, the reaction pathways in the reduction of most oxide systems comprise many individual steps and can only be elucidated experimentally [9].

The TiO₂ system has been investigated in detail [10,11], and there it was observed that, in the first stage of the process, fast reactions occur between the cathodically-polarised oxide and the molten salt that lead to the formation of Ti suboxides and calcium titanates in the cathode. These reactions are characterised by the

E-mail address: carsten@unizwa.edu.om.

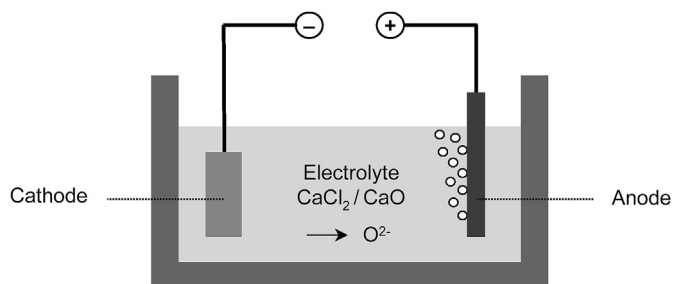


Fig. 1. Schematic representation of an FFC-Cambridge-type cell during the electro-deoxidation stage. The metal oxide cathode is electro-deoxidised, the molten salt electrolyte transports O^{2-} ions, and the carbon anode evolves CO/CO₂ gas.

incorporation of Ca^{2+} from the electrolyte into the cathode. The initial reaction step can be written as $5TiO_2 + Ca^{2+} + 2e^- = Ti_4O_7 + CaTiO_3$, and reaction steps of this type prevail up to the formation of a stoichiometric mix of TiO + CaTiO₃. These reactions are reductions because the electrons from the cathode lower the average oxidation number of the Ti, and they are not of a calciothermic nature because the Ca remains in the oxidation +2 throughout the reaction steps. The anode reaction is the release of Cl₂ in case the CaO content in the CaCl₂ melt is low [10], or the release of CO/CO₂ in case the CaO content is large enough to sustain the ionic current through the electrolyte [11]. At this stage of the process, the faradaic current is hence provided by electrode reactions involving two different types of ions from the melt, making the electrode reactions electrolysis-type ones. They proceed with a current efficiency of practically 100%, because no transport of electrons across the electrolyte and no backreactions between cathodic and anodic products are involved. Similar reaction patterns including the initial participation of Ca^{2+} ions from the electrolyte have also been found, for example, in the reduction of ZrO₂ [12], HfO₂ [13], Cr₂O₃ [14] and Nb₂O₅ [15], whereas no active participation of Ca^{2+} ions was found in the reduction of Fe₂O₃ [16] and UO₂ [17].

The second stage of the process starts governing once any reactions involving Ca^{2+} ions from the electrolyte are exhausted. The defining feature now is the actual electro-deoxidation, i.e., the generation of O^{2-} ions at the cathode, their transport through the molten salt electrolyte, and their removal at the anode. At this stage of the process, the faradaic current is thus provided by O^{2-} ions alone via the redox system $O^{2-} = O + 2e^-$, and the electrode reactions are no longer electrolysis-type ones. They too proceed with a current efficiency of practically 100%, because they are entirely ionic in nature and no backreaction is possible. The electrolyte is now electrochemically inert, with the CaCl₂ serving solely as the solvent for the CaO and thus for the O^{2-} ions.

The occurrence of the O^{2-} ion transport in an FFC cell during the stage of electro-deoxidation needs to be seen in the context of the thermodynamic stability of the CaO dissolved in the CaCl₂ melt as this is a requirement for such transport to be possible. In practice, most FFC experiments are performed in a two-terminal cell, in which a voltage of around 3 V is applied between the oxide cathode and the carbon anode, still in keeping with the procedures presented in the first publication on this subject [1]. As can be calculated from thermodynamic data [2], the decomposition potential of CaO dissolved in CaCl₂ at 900 °C is 1.54 V for CO and 1.63 V for CO₂ formation at the anode, both for a CaO activity of unity, corresponding to the saturation mole fraction of 0.2 (20 mol%), and with pure liquid Ca and pure solid CaO as the reference states. Both values increase by 0.12 V when the CaO activity is at 0.1 which corresponds to the practically relevant mole fraction of 0.02 (2 mol

%). Superficially, this would suggest that CaO is unstable in the melt under typical operating conditions and is simply removed from it by electrolysis. However, by means of studies using three-terminal cells, with an oxide cathode, a graphite anode and a graphite pseudo-reference electrode, it was possible to compare the potentials of anodically-polarised graphite and of non-polarised graphite in a CaCl₂ melt containing small admixtures of CaO [11]. In this way, it was shown that when 3 V are applied between cathode and anode, the anode overpotential alone amounts to around 1.5 V. By impedance spectroscopic analysis, it was furthermore shown that the resistance in the current collectors is around 0.2 Ω for Ni wires, and thus even bigger in other set-ups where steel or even Kanthal are often used. Altogether, the effective potential difference remains below the thermodynamic decomposition potential of CaO. Therefore, CaO can exist in the melt and enable O^{2-} ion transport in experiments performed at 3 V.

A further phenomenon to be considered in an FFC cell is that of electronic conduction through the molten salt electrolyte. It has its origin in the solubility of Ca in CaCl₂, which is around 3.7 mol% at 900 °C [18]. Consequently, each cathode potential corresponds to a finite activity of Ca in the CaCl₂ even at potentials more positive than that for Ca metal deposition. This Ca activity is lower than unity but larger than zero. It manifests itself in the presence of Ca_2^{2+} species that enable the transfer of electrons across the electrolyte [19,20]. While there is a small contribution of electronic conduction in all FFC experiments, this becomes especially adverse when thermodynamically very stable oxides, such as TiO₂, are processed under conditions close to Ca deposition. In such cases low residual oxygen contents and high current efficiencies are mutually exclusive [11].

The objective of this article has been to identify the correct physical expressions for the ionic transport in the molten salt electrolyte during the electro-deoxidation stage of the FFC-Cambridge process, and to draw conclusions on the electric potential distribution within the electrolyte. The results of these considerations have then been used to evaluate the general practicability of an FFC cell and to assess the soundness of the existing mathematical models for the ionic transport in FFC cells.

2. Nernst-Planck equation

Transport of charged particles in a fluid phase can occur as the result of a concentration gradient, i.e., via diffusion, an electric gradient, i.e., via migration, and a pressure gradient, i.e., via convection. Convection can be divided further into natural and forced; the former occurring due to density gradients caused by concentration or temperature differences; the latter occurring due to external sources such as propeller agitation, electrode rotation or gas sparging. Transport is subject to the conservation of mass, and this is expressed by the Nernst-Planck equation for the superposition of diffusion, migration and convection [21]; where c is the concentration [mol m⁻³], t is the time [s], and j is the particle flux [mol m⁻² s⁻¹]; D is the component or self-diffusion coefficient [m² s⁻¹], z is the charge number of the mobile charge carrier, F is the Faraday constant [A s mol⁻¹], b is the mechanical mobility [mol m² J⁻¹ s⁻¹ = mol m² V⁻¹ A⁻¹ s⁻²], ϕ is the electric potential [V], v is the fluid velocity [m s⁻¹], and u is the electrical mobility [m² V⁻¹ s⁻¹].¹

$$\frac{\partial c}{\partial t} = -\nabla j = \nabla[D\nabla c + zFcb\nabla\phi + cv] = \nabla[D\nabla c + cu\nabla\phi + cv] \quad (4)$$

¹ The correlation between electrical mobility, mechanical mobility and component diffusion coefficient is given by the Nernst-Einstein equation, $u = zFb = \frac{zFD}{RT}$, where R is the universal gas constant and T is the absolute temperature.

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