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THE FFC CAMBRIDGE PROCESS FOR METAL PRODUCTION: PRINCIPLE, PRACTICE AND PROSPECT

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Abstract

The Fray-Farthing-Chen (FFC) Cambridge Process was patented in 1998 for low cost and clean electrochemical extraction of metals and synthesis of alloys directly from the mineral precursors, particularly oxides (including slags) and sulfides, with the aid of molten salts. This paper explains this unique metal production method from the basic electrode reaction thermodynamics and mechanisms at the compound | metal | electrolyte three-phase interlines (boundaries). Selected recent innovations are then introduced towards more efficient cathode design and practices. Finally, the prospects of the FFC Cambridge Process are discussed for processing ilmenite ore to produce Fe-Ti alloys and its commercial potential in the future titanium industry.

Introduction

Metal oxides are the main components of many minerals and slags involved in industrial production of metals. Steels and aluminium are the two major structural metals extracted from their oxide minerals, although the methods used in the current industrial extraction of these two metals are completely different. Steels are extracted by carbothermic reduction whilst aluminium by electrolytic reduction. This is because the reduction power of carbon is insufficient to reduce alumina as reflected by the reactions below and the associated values of the Gibbs free energy changes at industrially meaningful temperatures (*e.g.* 1700°C).[1]

$$2\ Fe_2O_3 + 3\ C \rightleftharpoons 4\ Fe + 3\ CO_2 \qquad \Delta G^o = -555.2\ kJ \qquad (1)$$

$$2\ Al_2O_3 + 3\ C \rightleftharpoons 4\ Al + 3\ CO_2 \qquad \Delta G^o = 894.5\ kJ \qquad (2)$$

However, carbothermic reduction is at present much cheaper than electrolytic reduction because of the relatively lower cost of carbon in comparison with that of electricity. The main concern over carbothermic reduction is CO_2 emission. For example, at an annual production of over 1.4 billion tonnes world-wide,[2] steelmaking

should have corresponded to 830 million tonnes of CO_2 emission. However, due to process inefficiency, the industry actually emits 1.9 tonne CO_2 on average for producing each tonne of steel, accounting for up to 5% of the total global CO_2 emission.[3] In addition to environmental impact, the financial advantage of carbothermic steelmaking is expected to diminish soon with the fast exhaustion of fossil resources. Meanwhile, electricity production is expected to transfer from combustion of fossil fuels to conversion of the more sustainable renewables, particularly solar energy. This inevitable transition of energy supply will force the metallurgical industry to take urgent actions to either accept existing or develop new and efficient electrolytic processes.

In fact, even in the current industrial practice, electrolytic extraction of metals is still not satisfactory in terms of environmental impact, technology advancement and sustainability. Aluminium extraction is achieved via the Hall-Héroult process in which electrolysis proceeds at 900 ~ 1000°C in molten cryolite (Na_3AlF_6) which can dissolve alumina readily. The process uses a carbon anode on which the discharge of the oxide ion produces CO_2. Therefore, the chemistry of the Hall-Héroult process is essentially the same as reaction (2). Up till now, the global production of aluminium has reached over 40 million tonnes annually.[2] This converts to about 50 million tonnes of CO_2 emission according to reaction (2). It is worth highlighting that the modern version of the Hall-Héroult process, with the current efficiency reaching over 90%, is far more efficient than the carbothermic steelmaking process.

In terms of technology development, it is unfortunate that only aluminium and a few rare earth metals of low melting points are produced by electrolysis in molten salts.[4] Past attempts to produce other reactive and refractory metals, such as titanium and niobium, via molten salt electrolysis have all failed to meet commercial demands. It is worth mentioning that after the commercial success of the Hall-Héroult process in the 1950s, electrolytic extraction of refractory metals, particularly titanium, in molten salts was advocated by many researchers, including William Kroll whose invention is still in use in the modern titanium and zirconium industry. There are various problems encountered,[5-7] and two of these are highlighted here. Firstly, unlike aluminium which has a low melting point (660°C) and is produced as a liquid in the Hall-Héroult cell, the melting points of most refractory metals are much higher than the boiling points of the molten salts used. Thus, the metal has to be deposited as a solid on the cathode. Due to the anisotropic nature of crystal growth, the deposited metal tends to become a dendrite which may fall off the electrode, short circuit the cell, or be oxidised readily upon exposure to air or water. Secondly, most refractory metals have three or more valences. Thus, when dissolved in the molten salt, the multivalent metal ions can undergo redox cycling between the anode and cathode, which lowers the current efficiency.

In late 1990s, it was discovered in Cambridge that solid titanium dioxide (TiO_2) could be electrochemically reduced directly to titanium metal in molten $CaCl_2$, and this finding was soon realised to be generic to many metal compounds, particularly oxides and sulfides.[8,9] A novel metal extraction process was then proposed and named after the inventors as the Fray-Farthing-Chen (FFC) Cambridge Process. In the process, the mineral precursor (metal oxide, sulfide or other types of compound) is first made into a porous preform (*e.g.* small cylindrical pellet), attached to the cathode, and then placed in the molten salt together with a suitable anode (see more detailed discussion below). Under a sufficiently high cell voltage (but not too high to decompose the molten salt), oxygen (or sulphur) in the solid mineral precursor simply ionises, leaves the cathode, enters the molten salt, and discharges at the anode. Contrary to previous attempts, in the FFC Cambridge Process, no dissolution of the mineral and no deposition of the metal are needed. Instead, the porous mineral precursor is simply "metallised" in solid state on the cathode with the aid of molten salts, avoiding the problematic dendrite deposit and redox cycling.

In the past decade, the FFC Cambridge Process has been demonstrated by many researchers for production of various metals (*e.g.* Ti, Si, Cr, Tb, Mo, and Cu [9-14]) and alloys (*e.g.* Fe-Ti, Nd-Co, La-Ni, Ce-Ni-Cu, Zr-Cr-Ni [15-19]). The as-produced metal from the FFC Cambridge Process usually retains the shape of the mineral precursor with some shrinkage in dimensions. It is also possible to control the process conditions to achieve a powdery, porous or dense metal product. In practice, the FFC Cambridge Process may be realised in several ways, and one of these is shown in Figure 1 which is slightly modified from an early process design proposed by the author.[11]
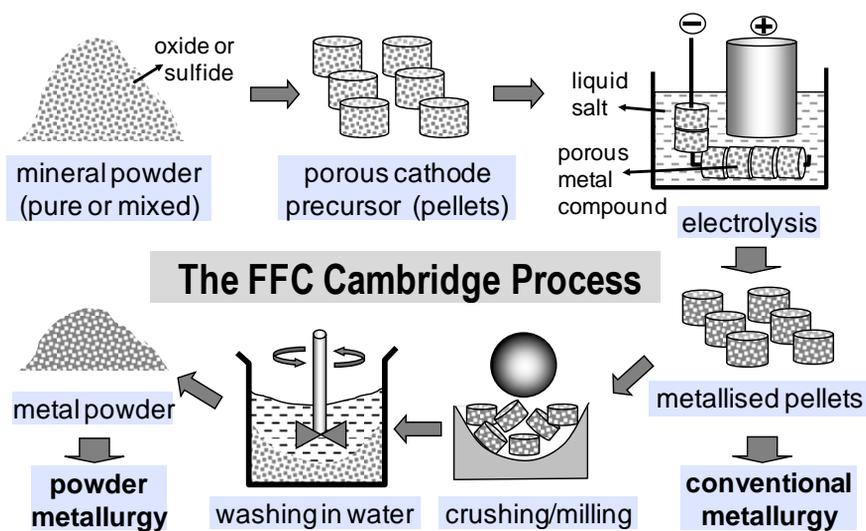
Figure 1: A schematic illustration of the FFC Cambridge Process for metal extraction by electrochemical reduction of solid mineral precursors in liquid salts (a collective term for high temperature molten salts and room temperature ionic liquids)[11]

Principle

Selection of electrolytes

Like many electrolytic processes, the FFC Cambridge Process takes place in a liquid electrolyte which is however unique in at least three ways. **Firstly**, it not only conducts ionic current in a wide temperature range, but also dissolves and transports the anions, such as O^{2-}, S^{2-} or Cl^-, that are formed in the electrochemical reduction (or simply electro-reduction or electro-deoxidation) of the solid compound on the cathode. **Secondly**, the electrolyte should have no solubility, or as small as possible, for the compound to be reduced. **Last**, but not the least, the potential window of the electrolyte, particularly the cathodic limit, needs to be sufficiently wide so that the reduction of the solid compound occurs before decomposition of the electrolyte.

Based on earlier research on metal refining,[20,12] molten $CaCl_2$ was the first electrolyte selected and tested for electro-reduction of TiO_2 at 950°C.[9] This high temperature approach has been followed in many reported studies on the reduction of various oxides of refractory metals.[10-19] In addition to pure $CaCl_2$, LiCl and $BaCl_2$ are the other two pure chloride salts capable of accommodating the FFC Cambridge Process for reduction of metal oxides.[7,22,23] This is because these three molten chloride salts can all dissolve and transport oxide ions (O^{2-}) to significant levels. Mixtures of these and other chloride salts, such as KCl and NaCl, were also used to achieve electro-reduction of metal oxides at lower working temperatures.

For electro-reduction of metal sulfides (or electro-desulfidation), both molten $CaCl_2$ and $BaCl_2$ were confirmed to be suitable.[13,14,22] An interesting and useful finding from studies of electro-desulfidation is that the graphite anode, which is a consumable in electro-reduction of metal oxides, function as an inert anode.[13,14] Of greater importance, it was demonstrated that pure molten NaCl or KCl, and their mixtures, which have very low solubility for the O^{2-} ion, could also be used for efficient electro-desulfidation coupled with a graphite inert anode.[24]

In recent reports, some fluoride salts were applied to support the FFC Cambridge process for electro-reduction of metal oxides,[25] although the toxicity of these salts may cause environmental concerns if used at large scales. Molten carbonate salts were also studied with a metallic inert anode.[26] Development of the FFC Cambridge Process in carbonate melts may technically benefit greatly from the historical interests and development in molten carbonate fuel cells.[27-29] Nevertheless, these environmentally benign melts could only help reduction of oxides of less reactive metals, such as iron. This is because electro-reduction of carbonate ion (CO_3^{2-}) to carbon as a deposit on the cathode occurs at potentials much more positive than that for the reduction of most reactive metal oxides.[26,30]

Apart from high temperature molten salts, attempts were also made to use either aqueous electrolytes or ionic liquids for electro-reduction. It is well known that electro-reduction of solid AgCl to Ag metal can proceed in an aqueous or organic electrolyte, which is the basis of the widely used Ag/AgCl reference electrode. This water-insoluble chloride was used as a model compound to study the kinetics and dynamics of electro-reduction at the compound/metal/electrolyte three-phase interlines[31,32] which will be discussed in details below. A relevant effort succeeded to electrolytically decompose suspended hematite (Fe_2O_3) particles to metal iron on the cathode and oxygen gas on the anode in concentrated NaOH at 114°C.[33] It was further confirmed that when attached to the cathode as a thin film, the fcc Fe_3O_4 could be electro-reduced to the bcc iron film in 2 M NaOH at room temperature.[34] The research effort at room temperatures was extended to using ionic liquids, also known as room temperature molten salts, for electro-reduction of solid cuprous chloride to copper nanoparticles.[35] It is nevertheless noted that all research attempts at room temperature have not worked for compounds of refractory metals, suggesting either or both of thermodynamic and kinetic difficulties.

Thermodynamic and mechanistic considerations

Because of their simpler composition, molten salts can be readily decomposed by electrolysis to pure elements which can be used as the references for thermodynamic studies. This is an advantage over electrolysis in aqueous electrolytes in which parasitic reactions are inevitable. Indeed, molten salt electrolysis is one of the earliest methods used for determination of thermodynamic properties of compounds.[36] In the FFC Cambridge Process, the compound on the cathode and the electrolyte composition are defined to sufficient clarity. The anode can also be assumed (and practically verified) to be either reactive or inert. In the following discussion, molten $CaCl_2$, TiO_2 and Fe_2O_3 are selected as examples for thermodynamic calculations using the commercial programme, HSC Chemistry.[1]

In molten $CaCl_2$, electrolysis of TiO_2 or Fe_2O_3 may bring about electrode reactions as listed in Table 1, depending on the applied voltage and the reactivity of the anode material. The anode material may be carbon based (*e.g.* graphite) or inert such as SnO_2 or the $CaRuO_3/CaTiO_3$ composite.[37,38] Of the listed reactions, (1) and (7) are from decomposition of molten $CaCl_2$, and one of these can be used as the reference. In the literature relevant to the FFC Cambridge Process, most authors used the electrode potential of (1) as the reference, i.e. E^o (Ca/Ca^{2+}) = 0 V. For the decomposition reactions of $CaCl_2(l) \rightleftharpoons Ca(l) + Cl_2(g)$ and $CaO \rightleftharpoons Ca(l) + 0.5\ O_2(g)$ at 900°C, the Gibbs free energy values are, ΔG^o ($CaCl_2$, l) = 667.413 kJ and ΔG^o (CaO) = 486.359 kJ, respectively. Following the equations of $\Delta G^o = nF\Delta E^o$ (F = 96485 C / mol), and $\Delta E^o = E^o$ (anode) - E^o (cathode, reference), it can then be calculated that E^o (Cl^-/Cl_2) = 3.459 V, and E^o (O^{2-}/O_2) = 2.520 V. Similarly, the electrode potentials for (2),

(3) and (6) can be calculated by coupling with (1) and (6) to establish the respective overall cell reactions. For example, for (5b), the overall reaction can be written as 2 CaO + C $\rightleftharpoons$ 2Ca(l) + CO_2(g) with ΔG^o = 576.679 kJ and ΔE^o = 1.494 V. If CaO dissociates completely to Ca^{2+} and O^{2-} before saturation in molten $CaCl_2$, it is reasonable to assume E^o (Ca/Ca^{2+}) $\approx$ E^o (Ca/CaO). Thus, E^o (C/CO_2) = 1.494 V.

Table 1: Electrode potentials (vs. Ca/Ca^{2+}) in molten $CaCl_2$ at 900°C

No.	Reaction	Electrode	Potential
(1)	Ca^{2+} + 2 e $\rightleftharpoons$ Ca(l)	Cathode	0 V
(2a)	$Ti_{1.5}O$ $\rightleftharpoons$ 1.5 Ti + O^{2-}	Cathode	0.283 V
(2b)	$CaTiO_3$ + 4 e $\rightleftharpoons$ Ti + CaO + $2O^{2-}$	Cathode	0.396 V
(3)	TiO_2 + 4 e $\rightleftharpoons$ Ti + 2 O^{2-}	Cathode	0.623 V
(4)	Fe_2O_3 + 6 e $\rightleftharpoons$ 2 Fe + 3 O^{2-}	Cathode	1.628 V
(5a)	O^{2-} + C $\rightleftharpoons$ CO(g) + 2 e	Anode (carbon)	1.404 V
(5b)	2 O^{2-} + C $\rightleftharpoons$ CO_2(g) + 4 e	Anode (carbon)	1.494 V
(6)	2 O^{2-} $\rightleftharpoons$ O_2(g) + 4e	Anode (inert)	2.520 V
(7)	2 Cl^- $\rightleftharpoons$ Cl_2(g) + 2 e	Anode (inert)	3.459 V

Table 1 shows that the electrode potential of (4) is more positive than those of (5a) and (5b), suggesting spontaneous reactions if the Fe_2O_3 cathode is coupled with a carbon anode which is expected. Further, both (3) and (4) represent the overall change on the cathode, but there are in fact mechanistic and kinetic complications. For example, it has been demonstrated that electro-reduction of TiO_2 in molten $CaCl_2$ goes through the Magneli phases (Ti_nO_{2n-1}, 3 ≤ n ≤ 10),[9,39,40] the perovskite phases ($Ca_\alpha TiO_\beta$, α ≤ 1, 2 < β ≤ 3),[41-43] and the metallic pseudo-oxide phases (Ti_mO, 1 < m ≤ 6),[44-46] before arriving at the titanium phase with a sufficiently low content of oxygen. Particularly, reduction of these perovskite and metallic pseudo-oxide phases, *e.g.* (2a) and (2b) in Table 1, occurs at more negative potentials than that of (3).

The three-phase interline model

It is a common perception that an electrolytic cell should be constructed from either electronic or ionic conductors, except for regions where the current flow should not occur. Thus, it was surprising that solid TiO_2 which is effectively an insulator could be directly electro-reduced to Ti metal.[9] The cause was initially related to the formation of the more conducting Magneli phases. However, electro-reduction of the insulator SiO_2 to pure Si also succeeded partially on silica glass,[10] and completely on silica powder,[47] even though there is no intermediate phase between SiO_2 and Si. ZrO_2 is another an insulator but has been successfully reduced to Zr metal without involving an intermediate phase containing Zr at lower valences (*e.g.* II and III).[48]
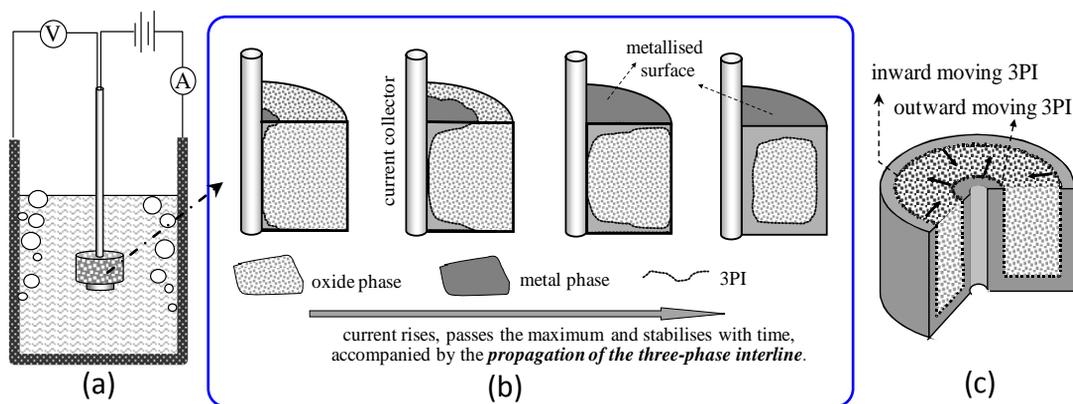
Figure 2: Schematic illustration of (a) a cell for electrolysis of a suspended oxide pellet in molten salt, and (b) 3PI propagation along the surface, and (c) within the pellet[11]

The attention was then paid to the meal/oxide/electrolyte three-phase boundary.[49,50] Because the boundary linking three different phases can only be a line (or a point), it is called the three-phase interline or 3PI. Figure 2 explains the experimentally observed progression of electro-reduction of a cylindrical porous oxide pellet. For clearer illustration, only a portion of the pellet is drawn. The pellet is suspended in the molten salt with a metal wire (current collector) through a hole in the pellet's axial centre. At the beginning of electrolysis, the 3PI is only present between the metal wire, oxide and molten salt. Upon electron transfer, the oxide next to the metal wire is reduced to the metal, which expands the 3PI. Further reduction then occurs at the newly formed 3PI. Because the reduction removes O^{2-} ions via diffusion through the molten salts, the 3PI propagation is fastest on the pellet's surface that is in contact with the bulk electrolyte. After the whole surface is reduced, the 3PIs then propagates into the pellet.

The 3PI model was further verified theoretically and experimentally through electro-reduction of AgCl as the model compound in aqueous electrolyte.[31,32] Based on the 3PI model, further understanding of the FFC Cambridge Process has been developed, including the recognition of the influence of the metal-to-oxide molar volume ratio,[45] and the correlation between the highest electro-reduction rate and the optimal porosity of the oxide cathode as determined by the equation below,

$$P_{opt} = \frac{3R + S - 1}{3R} \times 100\%$$ (3)

where P_{opt} is the optimal oxide precursor porosity in volume percentage, R the metal-to-oxide molar volume ratio, and S the cathode volume shrinkage in volume fraction.

This simple relationship, called the PRS model, agrees very well with experimental studies of the electro-reduction of TiO_2, Ta_2O_5 and SiO_2 in molten chloride salts.[49]

Practice

In the past decade, great efforts and significant progresses have been made world-wide in fundamental research and commercial development of the FFC Cambridge Process.[6,7,50] In practice, various electrode, cell and process designs and analytic methods have been applied to study the process. These are highlighted as follow.

Process control

Temperature: The FFC Cambridge Process was first demonstrated in both the three-electrode cell (with a Ti metal pseudo-reference electrode) and two-electrode cell in molten $CaCl_2$ under argon. The melting point of $CaCl_2$ is about 780°C, depending on the purity. Thus, the working temperature of molten $CaCl_2$ was varied between 800°C and 950°C. Further increasing the temperature causes salt evaporation,[22] although $CaCl_2$ would not boil below 1600°C. Again, faster electro-reduction was observed at higher temperatures. It is worth mentioning that the process should not be operated under air or vacuum to avoid (1) contamination of the product by oxygen, and in some cases, nitrogen, or (2) evaporation of the chloride salts. The salt vapour can condense in, and block the gas outlet of the reactor, and is also very hygroscopic and corrosive to laboratory equipment.

Voltage: In the two-electrode cell, the electrolysis was typically carried out under constant voltage control, although constant current control was also used for understanding electrode reactions.[51] The upper limit of the electrolysis voltage was set to be high enough to reduce the metal oxide (compound), but also to avoid decomposition of the molten salt. For molten $CaCl_2$, the voltage control follows the data in Table 1. The electrolysis rate increases with the cell voltage, but the current efficiency does not always follow the same trend. Another factor affecting the current efficiency is electronic conduction which is common in molten salts containing dissolved metal and/or cyclic redox reactions, and increases with voltage.[52-54] In the following discussion, the focus is on molten $CaCl_2$ which is mostly used in research as reported in the existing literature.

Electronic conduction was found to be more serious in molten $CaCl_2$ than in for example, molten $BaCl_2$.[22] This difference is at least partly due to $CaCl_2$ being more hygroscopic than $BaCl_2$, which means that there is likely more CaO in molten $CaCl_2$ than BaO in molten $BaCl_2$ after thermal drying as explained here. In general, chlorides of alkali and alkaline earth elements are hygroscopic in nature, and require pre-

drying the salt granules before melting. This can be achieved by a three stage heating programme for treatment of typically up to 1 kg of the salt granules. Firstly, quickly raise the temperature (*e.g.* 10°C/min) to 150°C in air to evaporate most physically absorbed water in ca. 1 h. Secondly, slowly heat to 270°C (*e.g.* 0.2°C) to remove chemically bonded or hydrated water for up to 5 h. Finally, place the salt in the sealed reactor that is purged with argon, and increase the temperature (*e.g.* 10°C/min) to 700°C for ca. 1 h before melting.[22,55]

Moisture in molten salts is redox active and can contribute to lowering the current efficiency and also cause hydrolysis such as $CaCl_2 + H_2O \rightleftharpoons CaO + 2 HCl(g)$. Careful thermal drying as introduced above can help to remove a great amount of water in the salt, but is practically challenging to achieve completion in air or even an inert gas. More complete drying may be achieved by thermal drying under the HCl gas, which is not preferred consider the safety regulations in laboratories nowadays. Pre-electrolysis (*e.g.* 2.5~2.8 V and 1~5 h in 1 kg of molten $CaCl_2$ under argon) has been applied in the author's work to achieve satisfactory removal of the moisture without compromising safety. The added benefit of pre-electrolysis is that it can also remove other redox active impurities such as the Mg^{2+} ions with a nickel cathode.[56]

Because electro-reduction of metal oxides always discharges O^{2-} from the cathode into the molten salt, a small amount of CaO from hydrolysis is not a problem. It can in fact help avoid anodic discharge of Cl^- ions in the initial period of electrolysis. However, too high a concentration of CaO can cause a large back ground current, particularly when the cathode was mostly metallised, due to CaO decomposing at a lower voltage than $CaCl_2$, see Table 1. The optimal initial CaO concentration should correlate with the maximum current passing through the cell during electrolysis. It obviously depends on the total amounts of metal oxide on the cathode and of the molten $CaCl_2$ in the cell. An effective practice is to start with a CaO concentration as low as possible, and allow the electrolysis to generate CaO by discharging some the Cl^- ions in the initial period of electrolysis of the metal oxide.

Time: Electrolysis time is an important variable for control of the oxygen content in the produced metals. For electrolysis of ca. 1~3 g of pellets of metal oxides, the time was typically less than 10 h for less reactive metals, such as Cr and Fe, but much longer for Ti and Nb. Because of the relatively high background current, a longer time of electrolysis means a lower current efficiency. For example, for electrolysis of a 1~2 g pellet of Cr_2O_3, 6 h electrolysis at 2.8 V and 950°C is sufficient to achieve low oxygen content (< 2000 ppm) with the current efficiency being higher than 75%. [11] A similar experiment for TiO_2 would take a much longer time with the current efficiency dropping to below 15%.[41,57] An important theoretical development in electro-reduction is the correlation of the electrolysis efficiency (speed) with the

metal-to-oxide molar volume ratio and the cathode structure (porosity).[45,49] This correlation requires a porosity of ca. 68% in a TiO_2 pellet of 2~3 mm in thickness to achieve fastest reduction rate, which was well verified experimentally.

Cell and electrode

The first demonstration of the FFC Cambridge Process used both the three-electrode cell (for electrochemical analysis with a Ti metal pseudo-reference electrode) and two electrode-cell (for demonstration and also preparation of sufficient amounts of products) in molten $CaCl_2$ at 800 ~ 950°C under argon. Several materials have been used for fabrication of the electro-reduction cell, including titanium, graphite, steel (stainless) and alumina. Silica is not recommended because of its vulnerability to chemical attack by, for example, CaO and Ca metal at elevated temperatures.

Titanium is a highly effective material due to its ability as a getter to lower the oxygen content in the reactor, which is needed for reducing oxides of highly reactive metals, such as Ti and Zr. However, graphite which also can react with oxygen offers a satisfactory and much cheaper alternative for making reactive metals. Alumina crucibles were used successfully to produce less reactive metals, e.g. Cr and Si.[11,47] Stainless steel crucibles were used to producing Cr[11] and can be used repeatedly. The main concern is product contamination by Fe, Ni, and, to a lesser degree, Cr which are discharged into the molten salt from the stainless steel crucible.

In early electro-reduction experiments,[9] the working electrode or cathode was a TiO_2 thin layer coated titanium foil, or small porous cylindrical pellets of compacted TiO_2 powder. The counter electrode or anode was a graphite rod whilst the molten salt was contained in a titanium cup (crucible). In the follow-on studies since 2000, many changes have been made to these early experimental settings. However, the pellet design remains the choice for electro-reduction of many metal oxides and sulfides in the two-electrode cell. Fabrication of the pellet from the oxide powder in laboratory research is usually via either die-pressing or slip casting, followed by sintering at elevated temperatures (e.g. 900 ~ 1000°C for TiO_2). Polymeric binder may be used to increase the strength of the as-formed pellet for handling and can be burned out during sintering. The pellet cathode design enabled a recent in-situ investigation of electrolysis of TiO_2 by synchrotron diffraction, revealing very valuable information.[58] In addition to benefits to electro-reduction, the selection of pellets based cathode is to take advantage of the fact that pelletising technologies are widely used in commercial products related with, for example, minerals, biomass and medicines.

Attachment of the metal compound (oxide or sulfide) to the cathodic current collector can be achieved via several ways, and some are illustrated in Figure 3. Note
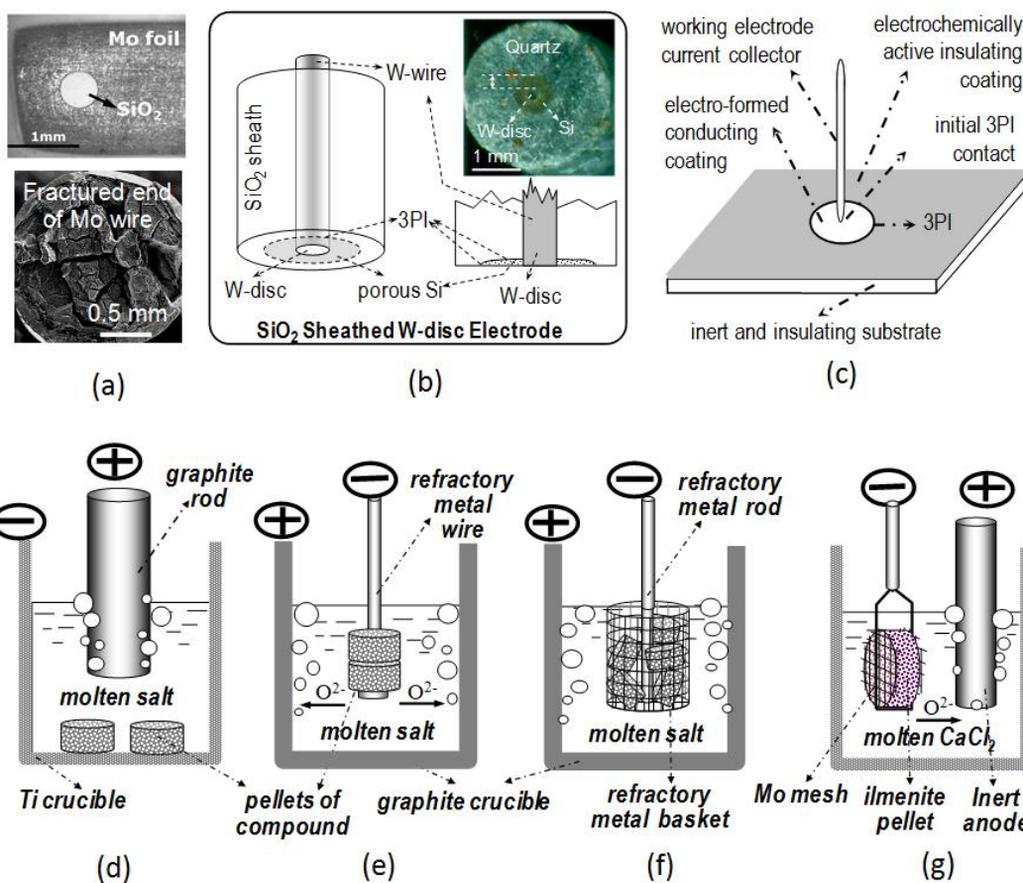
Figure 3: Selected laboratory and possible commercial cell designs for the FFC Cambridge Process with the cathode (working electrode) being the type of (a) powder-in-cavity (top: SiO_2 powder loaded in the through-hole of a Mo foil,[13,48] bottom: cracks in fractured end of Mo wire[41]), (b) disc-with-oxide-sheath,[47] (c) contact-pin,[10,31] (d) pellets-in-crucible,[9,11] (e) suspended pellet(s),[9,11] (f) pellets-in-basket,[3,58] (g) metal-mesh-wrapped-pellet.[15,41] It is possible to rearrange and recombine elements in each design for a new one to achieve particular purposes

that the electrodes in (a), (b) and (c), and the cells in (d) (e) and (g) are more suitable for laboratory investigations, but the basket cathode design in (f) was tested successfully by the author in a 1 kg-scale pilot test for commercial applications. The basket cathode was also modified to a planner type and investigated at the scale of 2.5~3.5 kg for electro-reduction of squared TiO_2 pellets.[59]

While most researchers used graphite as the anode for electro-reduction, it was long recognised that there is greater feasibility of developing an inert anode for molten chloride salts which are less aggressive that molten fluoride salts.

Prospect

The FFC Cambridge Process is now being developed for production of titanium and tantalum at scales of commercial significance by spin-out companies of the University of Cambridge that have been specially established for commercialisation of the FFC Cambridge Process.[50,59] Pending on commercial development, the process has shown a wide spectrum of opportunities to produce various energy related materials at low costs. For example, there is an increasing trend of using electro-reduction to reprocess spent nuclear fuels containing dominantly oxides of uranium and other actinides in molten salts.[23,62-64] Another example is the electro-synthesis of hydrogen storage alloy powders directly from the respective oxide mixtures.[15,60,61] A particularly interesting finding is that it is possible to electro-reduce TiO_2 to Ti_2O in the form of nano-powders that serve very well as a highly active and CO-immune support of Pt catalyst for electro-oxidation of methanol or CO.[65]

Although there is not yet any formally published study directly on processing and utilisation of slags via the FFC Cambridge Process, the fact that most slags are metal oxides based promises a bright future. Of particular relevance to this prospect is the utilisation of ilmonite and titanium-rich slags. Several investigations were recently reported on electro-reduction of mixed Fe_2O_3 and TiO_2, and also natural ilmenite (mainly $FeTiO_3$) in molten salts.[15,66-68] Figure 4 shows the SEM images of the natural and synthetic ilmonite powders and the respective electro-reduction products.[15]
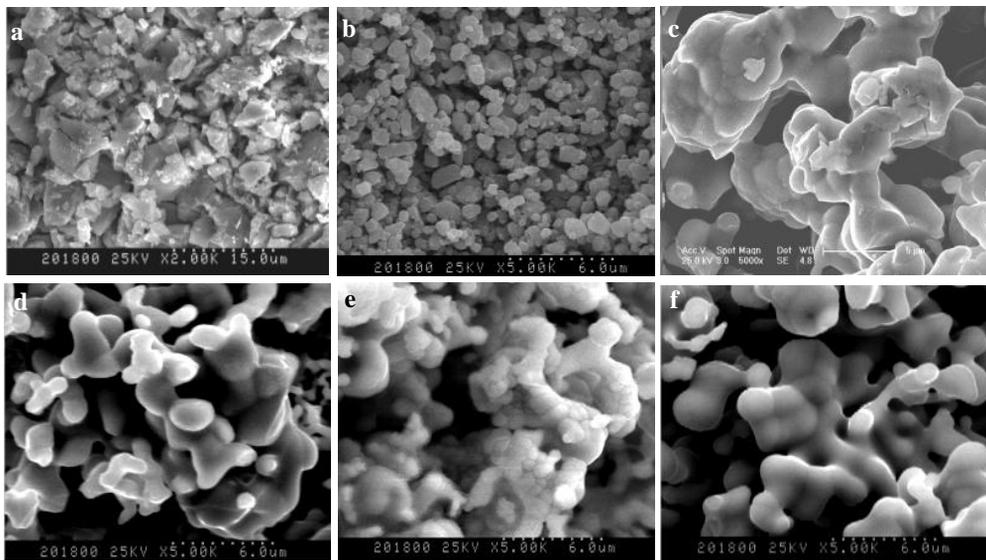
Figure 4: SEM images of (**a-d**) pressed and sintered powders of (**a**) ground natural and (**b**) synthetic limonite; their electrolysis products: (**c**) natural (900°C, 3.0 V, 12 h), and (**d**) synthetic (900°C, 3.0 V, 8 h), and (**e-f**) products from electrolysis (900°C, 3.0 V, 8 h) of (**e**) natural ilmenite + 4.46 wt% NiO (Ti = Fe + Ni) and (**f**) mixed TiO_2, Fe_2O_3 and NiO ($TiFe_{0.4}Ni_{0.6}$) [15]

Particularly for hydrogen storage, Ni was introduced into the product by addition of a suitable amount of NiO powder to the ilmenite powder before sintering. XRD analyses confirmed the electro-reduction products to be of the expected TiFe or $TiFe_xNi_y$ ($x + y = 1$) alloys.

It was observed that electro-reduction of ilmenite (or mixed Fe_2O_3 and TiO_2) started from the formation of pure iron, on which TiO_2 was reduced later to form directly the alloy.[15,66-68] According to this understanding, the energy released from the alloy formation should have contributed to lowering the cell voltage in comparison with that for the reduction of pure TiO_2. The actual energy consumption for reducing natural ilmenite was 14.4 kWh/kg-alloy at 3.0 V for 8 h, even though about 60% oxygen in the cathode was removed in the first hour.[15] Oxygen contents in products from electrolysis for 15 h reached below 300 ppm in Fe-rich products, and below 1000 ppm for Ti-rich products.[67] In comparison, the lowest energy consumption for electro-reduction of TiO_2 under similar conditions, to Ti with an oxygen content of 3900 ppm was 25 kWh/kg-Ti.[45]
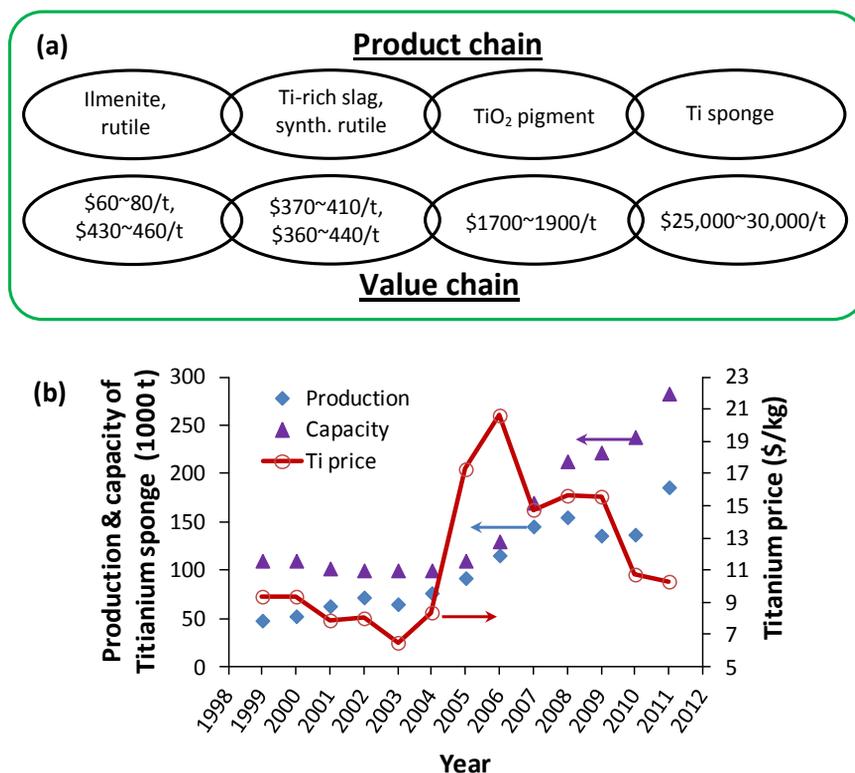
When changing the composition of the electrolytic Fe-Ti alloys, it was found that the products (after electric arc melting into ingots) reached highest hardness when Fe content was in the range from 15 to 50 wt%. These very hard products were also very brittle and should not be used for structural purposes. At other compositions, the products could be of commercial interests. Table 2 lists the Vickers hardness numbers (VHN) of the electrolytic Fe-Ti alloys as a function of the composition.

Table 2: Vickers hardness of products from electrolysis of mixed Fe_2O_3-TiO_2

Content of Fe_2O_3 (mol%)	0	0.9	2.2	3.6	70.8	89.2
VHN	120	389	583	687	399	237

When subjected to corrosion tests, the Fe-Ti alloys all exhibited excellent corrosion resistance in either simulated seawater (for Fe-rich products) or HCl solutions (for Ti-rich products). These properties are desirable for marine engineering applications.

Finally, it is worth pointing out that natural limenite is currently used as the feedstock for the so called "ilmenite smelting" or "titania semelting".[69,70] This is effectively a carbothermic reduction process, producing titanium rich slags as the main product and pig iron as a value added by-product. It is interesting to note the product chain and value chain of the current titanium industry as shown in Figure 5a. Although the market of titanium sponge has been volatile in the past decade as shown in Figure 5b, the large margin between TiO_2 pigment and Ti sponge offers great opportunities for the FFC Cambridge Process.

(a) **Product chain**

| Ilmenite, rutile | Ti-rich slag, synth. rutile | TiO$_2$ pigment | Ti sponge |

| \$60~80/t, \$430~460/t | \$370~410/t, \$360~440/t | \$1700~1900/t | \$25,000~30,000/t |

Value chain

Figure 5: (a) Schematic representation of the product chain and value chain as assessed in 2007,[69] and (b) the market trend of the titanium industry[2]

Summary

The development of the FFC Cambridge Process since its invention has been selectively reviewed in this paper. A wide spectrum of technological innovations and much improved fundamental understanding have come to light, thanks to the great efforts from researchers world-wide. Commercialisation in various areas, including processing slags, is becoming more feasible considering the predicted energy supply shifting from fossil fuels to renewables. With further technological and engineering progresses, the FFC Cambridge Process promises a great and bright future for a sustainable and affordable materials industry.

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