The FFC-Cambridge Process for Titanium Metal Winning

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Abstract. The FFC-Cambridge process is a molten salt electrochemical deoxidation method that was invented at the Department of Materials Science and Metallurgy of the University of Cambridge one decade ago. It is a generic technology that allows the direct conversion of metal oxides into the corresponding metals through cathodic polarisation of the oxide in a molten salt electrolyte based on calcium chloride. The process is rather universal in its applicability, and numerous studies on metals, semimetals, alloys and intermetallics have since been performed at the place of its invention and worldwide. The electro-winning of titanium metal is a particularly rewarding target because of the disadvantages of the existing extraction methods. This article summarises the research work performed on the FFC-Cambridge process at the University of Cambridge and its industrial partners with a focus on the electro-winning of titanium metal from titanium dioxide. Topics addressed encompass the invention of the process, early proof-of-concept work, the identification of the reaction pathway, and the investigation and optimisation of the key process parameters. Also discussed are aspects of technology transfer and some of the development work undertaken to date.

Background and Invention of the FFC-Cambridge Process

It is well known that titanium picks up oxygen when exposed to an oxygen-containing environment at elevated temperatures. In addition to forming an oxide coating, titanium is able to dissolve substantial amounts of oxygen to form an oxygen-rich metallic layer, called the alpha case, which has to be removed as its properties are inferior compared with the bulk metal. Removal of the surface layer of an artefact is usually achieved by either dissolving it in a mixture of nitric and hydrofluoric acids or by grinding it away. In both cases, the dimensions of the component change, and there are disposal problems with the generated waste.

In an approach to remove oxygen from titanium without invoking a change in dimensions, it was proposed that in a calcium chloride melt it should be possible to expel the oxygen by making the artefact the cathode. The suggested cathode reaction was:

Upon release from the titanium cathode, the oxide ions dissolve into the molten salt electrolyte, and then diffuse to the anode where discharge takes place. In order for the reaction in Eq. 1 to occur, two criteria need to be fulfilled. One is that the removal of the dissolved oxygen is possible at electrode potentials that are less cathodic than that for calcium deposition from the molten salt. The other is that the molten salt is able to dissolve oxide ions.

Laboratory experiments verified that it was indeed possible to deoxidise the surface of titanium samples with the proposed approach. Normally, the samples were exposed to the oxidising environment for a short time only but, in some cases, samples were exposed for many hours so that thick oxide coatings were formed. Rather surprisingly, these too were reduced by the electrochemical treatment. In an extension of Eq. 1, the suggested cathode reaction was:

This finding led directly to the proposal that by making an oxide the cathode in a bath of a halide of a very electropositive element, the oxide would be reduced. This was proven to be the case, and a patent has been granted on this new generic electro-deoxidation method [1]. A series of studies was initiated to attempt to understand how an insulating oxide could be reduced to a metal with low residual oxygen content [2-4].

One of the driving forces for the subsequent research was to determine whether this novel process of electro-deoxidation was likely to be competitive with conventional metal production processes. The direct conversion of titanium dioxide to titanium metal was deemed a particularly rewarding target because of the inherent drawbacks of the existing technologies like the Kroll and the Hunter processes. Also the possibility of forming alloys directly from the corresponding oxide mixtures was considered an attractive goal [5,6].

Studies on the Electro-deoxidation of Titanium Dioxide at Laboratory Scale

The overall cathode reaction in the reduction of TiO_2 to Ti by way of the FFC-Cambridge process is the removal of oxygen from the solid oxide cathode, while the titanium remains therein. The overall cathode reaction is given in Eq. 2. However, already in the early studies, a number of observations were made that gave clear indication of the kinetic pathway of the cathode reaction being more complex than what the simple overall reaction would suggest. Most notably, it was consistently observed that calcium-containing compounds like calcium titanate, CaTiO_3 , and, calcium titanite, CaTi_2O_4 , were present in the cathode partway through the reduction and that the cathode underwent a temporary mass gain.

Electro-deoxidation experiments with a two-terminal cell, constant potential, and low CaO concentration

The above observations prompted an in-depth investigation into the reaction pathway of the reduction of TiO_2 to Ti. The experiments in the first systematic study on TiO_2 reduction [7,8] were conducted by cathodically polarising TiO_2 discs, of 4 to 16 g in mass and with 25 - 30% open porosity, against a graphite anode in a CaCl_2 molten salt electrolyte at 900°C under argon. Fig. 1 presents a schematic of the electrochemical cell, and Fig. 2 shows a photograph of a typical laboratory set-up. Applied potentials were between -2.5 and -2.9 V and were maintained for different periods of time, ranging from 0.5 - 120 h, before reduction was interrupted by withdrawing the sample from the electrolyte. Importantly, in this set of experiments the CaO concentration in the CaCl_2 was low with values on the order of 0.2 mol%. The partially reduced samples were then subjected to a thorough examination using X-ray diffraction analysis, optical microscopy, scanning electron microscopy and energy-dispersive X-ray spectroscopy. The advantage of analysing partially reduced discs over, for instance, cyclic voltammograms from thin films, is that the former studies relate to conditions that would be applied in a scaled-up production process.

Fig. 1. Schematic of the electrochemical cell for electro-deoxidation experiments, showing the various components.

Fig. 2. Photograph of a typical laboratory set-up for electro-deoxidation experiments, showing metal retort, furnace, argon supply and electrochemical equipment.

Fig. 3 shows the initial phase of a current versus time curve recorded during a reduction experiment of the above type. There is an initial current peak, which extends over 1 h. This is followed by a current shoulder, which extends over a further 4 h. Finally the current assumes a rather small value, which remains relatively constant throughout the remainder of the experiment and only changes markedly when varying the applied potential.

Fig. 3. Current versus time curve recorded during an electro-deoxidation experiment of TiO_2 in a two-terminal cell; electrolyte: CaCl_2 ; cathode: porous TiO_2 disc of mass 8 g; anode: graphite; total applied potential: 2.5 V; temperature: 900°C ; atmosphere: dried argon.

It was concluded from Fig. 3 that the current during the initial peak would be too large to be sustained by oxide ions alone, since the CaO concentration in these experiments was low. This triggered the realisation that the first phase of the process is determined by the incorporation of calcium ions into the cathode. On the basis of information on phase composition, elemental composition and mass of the quenched samples as well as the amount of charge passed up to the point of terminating the experiment, the following sequence of cathodic reactions was derived:

In these reactions, the Ca^{2+} ions originate from the electrolyte and the electrons are injected from the negative terminal. It should be noted that the Ca^{2+} ions remain in the oxidation state of +2, and that no Ca metal is formed at any point in these reactions. The species to be reduced is the Ti ion. In the Ti-suboxide the Ti eventually reaches the oxidation state +3, while in the CaTiO_3 the Ti remains in its original oxidation state of +4. The current peak is of a comparatively short duration, indicating that the formation of the mixtures of Ti-suboxides and CaTiO_3 is kinetically facile. It was realised

that all the transitions between TiO_2 and Ti_2O_3 are fast because, as oxygen is removed, the type of oxygen coordination around the titanium remains intact, with the oxygen octahedra changing from corner-sharing to edge-sharing to face-sharing; nucleation and growth of the CaTiO_3 also occur rapidly.

The reaction during the current shoulder was again found to involve the incorporation of Ca ions into the cathode. Based on the experimental results, and in extension of the sequence above, the following cathodic reaction was identified:

The species to be reduced continues to be the Ti ion in the Ti-suboxides, which now reaches the oxidation state +2. The current shoulder is of significantly longer duration than the preceding current peak, indicating that the transition from Ti_2O_3 to TiO is kinetically more demanding than the foregoing ones. This is because the formation of TiO from Ti_2O_3 cannot occur via a simple shearing mechanism but requires a complete and comparatively slow reorganisation in the oxygen sublattice.

In the next phase CaTi_2O_4 becomes the dominant compound in the cathode. CaTi_2O_4 forms in large quantities from the mixture of TiO and CaTiO_3 . The following reaction accounts for this observation:

This reaction is entirely chemical in nature. Ti of oxidation state +2 in the TiO and Ti of oxidation state +4 in the CaTiO_3 comproportionate, forming CaTi_2O_4 with Ti in the oxidation state +3, thus leaving the average oxidation state of the Ti unchanged. Evidently the Gibbs free energy of formation of CaTi_2O_4 must be lower than the sum of those of TiO and CaTiO_3 , which allows this reaction to lower the energy of the system.

The subsequent phase is the breakdown of the CaTi_2O_4 to TiO. This is expressed by the following cathodic reaction:

This reaction step is critical for several reasons. Firstly, calcium incorporation into the cathode is no longer possible, and therefore the reduction must now involve the removal of oxygen, which gives rise to the formation of TiO with Ti in the oxidation state +2. Secondly, no compounds exist that contain Ca^{2+} ions as well as Ti in the oxidation state +2 and O^{2-} ions, and so the previously incorporated Ca must now be expelled from the cathode. Effectively this means that CaO is released from the cathode and if this occurs too quickly, there is a risk of locally saturating the CaCl_2 with CaO and hence stalling the process. Thirdly, the microstructural changes associated with this reaction step are dramatic, as will be discussed briefly below. Of particular note is the observation that, under the given conditions, the reduction of the CaTi_2O_4 progresses sluggishly. This was attributed to the low CaO concentration in the CaCl_2 which slows oxide ion transport across the electrolyte.

In the final phase the TiO is reduced to Ti with residual O dissolved in it. This is denoted by the following cathodic reaction:

This reaction provides the final product. It was found in the experiments that Ti with residual oxygen contents on the order of 3000 ppm by mass could be prepared, albeit after typical polarisation times of around 100 h or more.

Fig. 4. Scanning electron microscopic images of material occurring at different stages during an electro-deoxidation experiment of TiO_2 under the conditions specified in Fig. 3; (a) TiO_2 ; (b) $\text{Ti}_2\text{O}_3/\text{CaTiO}_3$; (c) CaTi_2O_4 ; (d) $\text{CaTi}_2\text{O}_4/\text{TiO}$; (e) $\text{Ti}[\text{O}]_\delta$. (Crosses indicate positions where elemental composition was measured.)

The above reactions are quoted with their standard electrode potentials E^0 . These refer to unit activities at 900°C and the Ca/Ca^{2+} standard, with pure liquid CaO as the reference state for the oxide, and have been calculated from known thermodynamic data. It is evident that the reactions become thermodynamically less favourable as the reduction proceeds but all of them require potentials less cathodic than that for Ca deposition. A few points are worthwhile noting. The reaction in Eq. 7 has no electrode potential as it is of a purely chemical nature. The standard electrode potential of the reaction in Eq. 8 cannot be calculated precisely as the Gibbs free energy of formation of CaTi_2O_4 is unknown, so only a limiting value may be given based on the fact that

CaTi_2O_4 is more stable than the individual compounds CaTiO_3 and TiO . Finally, when calculating electrode potentials under non-standard conditions, the concentration and the activity coefficient of the CaO need to be taken into account. The latter is 0.029 at the given temperature and for the given reference state. The quantitative change of the electrode potentials for different CaO contents may be considerable, but the general tendencies outlined remain valid.

As mentioned above, the microstructure of the cathode changes dramatically during the reduction of TiO_2 to Ti . Figs. 4a to 4e visualise the microstructural evolution. It is seen that the microstructures of the TiO_2 feed material and the Ti -suboxide/ CaTiO_3 mixtures are rather fine and dominated by interconnected spherical particles. The microstructure is then completely reconstructed twice. When the CaTi_2O_4 is formed, the microstructure becomes coarse and needle-like; and when the CaTi_2O_4 is broken down, the microstructure becomes fine again and is dominated by cuboid TiO particles. These then spheroidise to form the Ti product. The involvement of the CaTi_2O_4 in the reaction sequence is a critical feature of the reduction process. Firstly, the friability of the CaTi_2O_4 temporarily renders the cathode mechanically weak. Secondly, the breakdown of the CaTi_2O_4 bears the risk of the particles being formed becoming detached from the cathode. The Ti particles in the final product are globular with diameters of several micrometres and lightly sintered together, giving the typical sponge-type appearance. Obviously, the particles in the Ti product are much larger than those in the TiO_2 feed material, but in view of the intermittent changes, this must not be interpreted as plain particle coarsening.

The anode reaction in the FFC-Cambridge process is the discharge of oxide ions of the melt at a carbon based anode and the release of carbon oxides. The generation of CO_2 gas is preferred over CO gas due to the more efficient use of the consumable carbon anode and toxicity aspects. The generation of Cl_2 is undesired. Possible anode reactions and the corresponding standard electrode potentials are as follows:

It is seen that CO and CO_2 formation are thermodynamically favoured over Cl_2 formation. However, it should be recognised that Cl_2 formation is possible at potentials below the thermodynamic decomposition potential of CaCl_2 of 3.2 V at 900°C . This is a consequence of the reactive nature of the cathode, and becomes obvious when combining the electrode potentials for Eqs. 3 through 6 with that for Eq. 12. In the experiments it was indeed observed that a quantity of Cl_2 was liberated during the current peak. It needs to be considered further that the anodic release of carbon oxides is associated with significant polarisation losses on the order of 1 V, as determined in a separate study [9], whereas this is not the case for Cl_2 .

Unfortunately, current efficiencies in the experiments yielding Ti metal were only between 10 - 20%. This was attributed to the rather extended polarisation times at high applied potentials. As Ca is soluble in CaCl_2 , potentials somewhat below the decomposition potential of the electrolyte will give rise to the formation of a small amount of dissolved Ca in the electrolyte, and this imparts a degree of electronic conduction on the electrolyte that lowers current efficiency. In fact, the presence of dissolved Ca in the electrolyte is an undesired side effect, and not a requirement for reduction to go to completion.

Electro-deoxidation experiments with a three-terminal cell, ramped potential, and intermediate CaO concentration

The set of experiments summarised in the foregoing section provided fundamental insights into the reaction pathway of the reduction of TiO_2 to Ti. However, that study also revealed several deficiencies like the slow rate of reduction, the low current efficiency, and the possible generation of chlorine at the anode. These issues prompted a second in-depth study on TiO_2 reduction [10]. In this, a number of fundamental changes were made. Firstly, the CaO concentration in the CaCl_2 was increased to 2.0 mol% so as to enable higher transfer rates of oxide ions across the electrolyte. Secondly, a pseudo-reference electrode was incorporated into the cell in order to permit better control over the cathodic reactions and, in particular, to avoid unnecessary calcium deposition at the cathode. Through the combination of cathodic potential control and enhanced overall reaction rate it was furthermore endeavoured to improve current efficiency. Thirdly, a potential ramp was introduced at the beginning of the polarisation regime so as to eliminate large initial current peaks. This, in combination with the increased CaO concentration, should suppress chlorine formation.

The experiments were performed by cathodically polarising TiO_2 discs, of 2 g in mass and with 25 - 30% open porosity, and, as before, using a graphite anode, 900°C and argon atmosphere. However, potentials were now applied versus a pseudo-reference electrode of graphite. The appropriateness of such a surprisingly simple type of reference electrode had been validated before in a separate study [9]. Polarisation was commenced with a potential ramp of 300 mV/h, target potentials were between -0.8 and -1.6 V versus graphite and kept constant throughout the remainder of the experiment, and the overall duration was 16 h in each case. The samples prepared were then examined as before.

Fig. 5 shows a current versus time curve recorded during a reduction experiment of the above type. First the current increases with time and goes through two waves, then the current peaks, and finally it stabilises at a relatively high level. Overall, curves like the one on Fig. 5 have few salient features and are therefore of little analytical value.

Fig. 5. Current versus time curve recorded during an electro-deoxidation experiment of TiO_2 in a three-terminal cell; electrolyte: CaCl_2 with 2 mol% CaO; cathode: porous TiO_2 disc of mass 2 g; anode: graphite; reference: graphite; applied potential versus reference: 300 mV/h to -1.4 V; temperature: 900°C ; atmosphere: dried argon.

The reaction pathway was analysed primarily on the basis of phase composition, microstructure and elemental composition of the processed sample. On the whole, the conversion process was found to follow the same sequence of reaction, Eqs. 3 through 9, that was derived in the first study. The key finding in the second study was that the enhanced CaO concentration in the molten salt electrolyte led to a substantial increase of reaction rate, pointing to enhanced oxide ion transfer across the electrolyte. In addition, a number of new observations were made. While in the previous case oxygen removal only commenced after almost the entire cathode had been transformed into CaTi_2O_4 , now the direct conversion of Ti_2O_3 and CaTiO_3 to TiO at the edges of the sample was seen:

The earlier onset of oxygen removal has also been attributed to the improved oxide ion transport in the electrolyte. Despite the general acceleration of the reduction process, and especially the faster breakdown of the Ti_2O_3 and CaTiO_3 , copious amounts of CaTi_2O_4 were still found in the core region of the samples. It was suggested that the formation of the CaTi_2O_4 from TiO and CaTiO_3 is catalysed by the CaO dissolved in the CaCl_2 , suggesting that the intermediate presence of CaTi_2O_4 cannot easily be circumvented.

In addition to the general acceleration of the TiO_2 to Ti conversion in the second study, some additional improvements were identified. The utilisation of a reference electrode has provided improved process control. More specifically, the demonstration of Ti formation at potentials less cathodic than that of Ca deposition has provided further evidence for the general concept of the process. The combined use of a reference electrode and an increased CaO concentration in the electrolyte have furthermore enabled attaining improved current efficiencies of up to 40%. The combination of applying an initial ramp in the polarisation regime and increasing the CaO concentration in the electrolyte have rendered the reduction process essentially chlorine-free. Overall, the above conclusions demonstrate clearly that the CaO content of the electrolyte is a key parameter in the FFC-Cambridge process. Further to this, in the particular case of using a graphite based reference electrode, the CaO has another important function in that it defines the pseudo-potential of the reference electrode [9].

In summary, the in-depth studies into the direct electrochemical reduction of TiO_2 to Ti via the FFC-Cambridge process have provided a very detailed picture of the underlying fundamentals. It has been possible to derive a robust set of process parameters that ensures fast and efficient metal-to-oxide conversion and adequate process control in experiments performed at a laboratory scale. This demonstrates the huge potential of the method, and patent protection for a number of key findings has been sought [11].

Experiments on the Electro-deoxidation of Titanium Dioxide at Pilot Plant Level

Soon after the invention of the FFC-Cambridge process, British Titanium plc was founded as a Cambridge University spin-out company and granted a licence for the production of titanium and alloys containing more than 40 mass% titanium. Initial work on scaling up the process took place within the Department of Materials Science and Metallurgy of the University of Cambridge and at QinetiQ, taking production quantities from a few grams to around 1 kg of titanium dioxide per batch. The pilot plant in the University was designed in-house and consisted of an externally heated, circular stainless steel vessel, enclosing a steel crucible, a ring of carbon anode rods, and a central cathode holder that contained the oxide precursors in a perforated steel basket. The set-up is displayed on Fig. 6. The QinetiQ pilot plant was similar in design and throughput. British Titanium

took over the use of the University reactor in 2002 and eventually moved it to their premises in Cambridge. At the same time, design work was carried out to produce a larger capacity reactor.

Fig. 6. Photograph of a pilot plant for electro-deoxidation experiments, showing steel vessel, furnace, power supply and lifting equipment.

The first experiments using the University reactor were prior to the elucidation of reaction pathways and the realisation of the importance of specific control of the electrolyte composition and cathode potential. Nevertheless, it was possible to produce kilogram quantities of titanium with relatively low oxygen contents in some batches, although the results remained inconsistent. When metal was produced, current efficiencies were typically a few percent only. At the same time, considerable plating of dendritic metal deposits was found on the outside of the cathode holder originating from the metal components of the reactor.

The above observations led to the testing of the University reactor with a porous refractory ceramic liner. This led to metal production at much higher current efficiency of around 15% and without the high levels of dendrite formation on the cathode holder. However, cooling of the reactor following the experiments led to the cracking of the outer steel shell due to thermal expansion mismatch between the salt and the steel, so this reactor was no longer functional.

The next reactor design was a planar cell with anode and cathode facing each other inside a square steel chamber and retro-fitted with a refractory liner. Above the chamber for molten salt was a second argon purged chamber into which the cathode could be retracted, removed from the reactor, and replaced. This enabled the reactor to remain at temperature and avoid the possibility of the shell cracking on cooling. Similarly, the anodes could be replaced as required without cooling the reactor. This reactor typically processed 2.5 - 3.5 kg of titanium dioxide per batch. Figs. 7a and 7b show the custom-built cathode holder and the upper chamber. This design was conceived as being scalable with multiple cathode-anode arrangements producing many tens or hundreds of kilograms of material per unit.

Fig. 7. Photographs of components of a pilot plant for electro-deoxidation experiments, showing (a) the planar cathode holder; (b) the upper chamber that enables exchange of electrodes in argon atmosphere while maintaining the reactor at temperature.

In all, eleven experiments were conducted with the above reactor at temperature for over six months. Many, although not all, batches produced fully metallised product, the best oxygen content measured being 800 ppm by mass, with a current efficiency of approximately 28%. Extensive optical microscopy was carried out on the products of these experiments and those carried out in other, smaller, reactors and much discussion took place with members of the University. These confirmed the reduction mechanisms being proposed and led to the measuring and adjusting of the electrolyte composition, as well as the incorporation of a pseudo-reference electrode in the planar cell to monitor and control the applied potentials. This explained the inconsistencies in product quality for those experiments carried out under imperfect conditions in the earlier work.

British Titanium together with members of Cambridge University, had discussions with Norsk Titanium AS with a view to collaborating in the further development of the FFC-Cambridge process via a joint venture. Norsk Titanium had connections with Hydro which has extensive experience of molten salt based processes and laboratory facilities suitable for relevant experimental work. It was decided to conduct a number of experiments jointly with members of Hydro in their laboratories in Porsgrunn. These made use of a more sophisticated monitoring and control system than that used at British Titanium, enabling remote adjustment of the operating parameters. The culmination of this work was the successful reduction of a batch of titanium dioxide in less than one day by interactively controlling the applied potential throughout the experiment. This was done by producing a suitable polarisation regime relative to a pseudo-reference electrode, and confirming the efficacy of the pseudo-reference electrode by comparison to a more sophisticated reference electrode made available by Hydro. Shortly after this, at the end of 2005, the British Titanium licence was terminated and unfortunately this fruitful collaboration came to an untimely end, although it was likely to pave the way towards commercialisation of the process.

Other groups have also worked on scaling up the FFC-Cambridge process, particularly QinetiQ, BHP Billiton and Metalysis, who are currently working together. It is not clear from their presentations that in the four years since the termination of the British Titanium licence, their efforts to scale up the process have progressed this technology further than had been achieved through the close collaboration between Cambridge University, British Titanium and Hydro. Work at British

Titanium then focused on exploiting the FFC-Cambridge process for the production of oxygen from rocks by using inert anode technology, with a view to in-situ resource utilisation in extra-terrestrial areas. This programme was carried out in close collaboration with NASA.

Recent Research and Development Activities

Most of the work on the reduction of titanium dioxide via the FFC-Cambridge process was directed towards the production of titanium metal and titanium alloys in bulk quantities. In addition to this, several more specialised applications were envisaged. Two cases in point are the preparation of Ti coatings on steel through the reduction of deposited TiO_2 [12], and the preparation of highly porous Ti metal through the reduction of TiO_2 precursors containing fugitive additives [13]. These efforts were met with success and underscore the versatility of the process.

Arguably the biggest issues about operating the FFC-Cambridge process at a larger scale is the utilisation of a carbon based anode. Firstly, as carbon oxides are evolved and the anode is gradually consumed, particles of carbon can be eroded from the anode and build up as a sludge in the electrolyte, which can short-circuit the cell. Secondly, the CO_2 may dissolve as the carbonate ion, CO_3^{2-} , in the electrolyte. The CO_3^{2-} ions can diffuse to the cathode, where discharge and carbon deposition take place [9,10].

The carbon deposit may contaminate the product although usually it can be wiped away readily. The main concern is that this parasitic reaction results in a reduction in the current efficiency.

A study was undertaken of the various materials that have been tried in the aluminium industry as inert anodes, and these included metals, cermets and tin oxide. Without exception all the metals and cermets tested very quickly eroded when an anodic potential was applied in a chloride based electrolyte. The only exception was tin oxide that lasted about 50 - 100 h before an insulating layer of calcium stannate formed on the anode and essentially terminated the experiment [14].

In some reductions of TiO_2 it was noted that CaTiO_3 deposited as a separate phase on the graphite anode surface in the course of the experiment [10]. As CaTiO_3 is obviously stable in the chloride melt, it would make an ideal anode, except for the fact that it is a poor electrical conductor. It was first attempted to increase the defect concentration in CaTiO_3 by doping with oxides that have a cation with a different valence to that of the host cation. However, only modest improvements of the electronic conductivity could be achieved. A search of the literature then showed that calcium ruthenate, CaRuO_3 , which is an excellent metallic conductor, forms a complete solid solution with CaTiO_3 . As might be expected, the conductivity decreases as the proportion of CaRuO_3 in the solid solution decreases. At 10 mass% CaRuO_3 , the conductivity has fallen by a factor of 10^4 at room temperature. However, as the proportion of CaRuO_3 decreases, the conductivity of the solid solution changes from that of a metallic conductor to that of a semi-conductor. It is one of the properties of a semi-conductor that its conductivity increases with increase in temperature and it was found that at 800 - 900°C, the solid solution's conductivity was around $10 \Omega^{-1} \text{cm}^{-1}$ which would be satisfactory for an electrode material [15].

Electrodes composed of the solid solution of CaTiO_3 and CaRuO_3 were fabricated and tested in oxide reduction experiments in molten CaCl_2 based electrolytes. It was found that, provided there is about 1 - 2 mol% CaO in the melt, there was no erosion and the anodes were completely unaffected by the evolution of oxygen. The mass loss was $0.0015 \text{ g cm}^{-2} \text{ h}^{-1}$, which means that the anodes can be regarded as inert in these melts. It was also found that the $\text{CaTiO}_3/\text{CaRuO}_3$ anodes exhibit low polarisation losses for the oxygen evolution reaction. Therefore, the difference in anodic potential between O_2 release on $\text{CaTiO}_3/\text{CaRuO}_3$ and CO/CO_2 release on graphite was significantly less than the 1 V indicated by the thermodynamics. Overall, by using the new material, the CaCl_2 based melt remained white in appearance throughout the reduction experiments, and the current efficiency was

increased by about 10% compared with the use of graphite anodes [15]. It should be noted that ruthenium is a relatively expensive metal which would preclude the use of pure CaRuO_3 , but a dilute solution of CaRuO_3 in CaTiO_3 with a 10 mass% content of CaRuO_3 , corresponding to a 5 mass% content of Ru, is considered economically feasible. Again, patent protection is being sought [16], and large scale testing is envisaged in future work.

Overall, optimisation of processing conditions and utilisation of an inert anode has rendered possible the reduction of titanium dioxide to titanium metal via the FFC-Cambridge process within a timeframe of 14 - 16 h, a current efficiency of around 40%, and an energy consumption of around 17 kWh kg⁻¹.

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