



The production of oxygen and metal from lunar regolith

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ABSTRACT

The present article summarises the various methods that have been, and still are, explored for the production of oxygen from lunar materials. These include the classical concepts based on chemical reduction with hydrogen or methane, vapour phase pyrolysis, sulphuric acid treatment, and molten oxide electrolysis. Our main focus in this paper is on a novel approach developed at the University of Cambridge that employs molten salt electrochemistry to achieve the combined winning of oxygen and metal from solid lunar materials of varying composition. This makes the Cambridge process attractive because it will work equally well in mare as in highland regions. We also discuss the implications of the recent apparent discovery of water ice at the poles of the Moon and conclude that, even if this discovery is confirmed, it will nevertheless be desirable to provide oxygen at non-polar localities, and the Cambridge process is a strong candidate for achieving this.

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1. Background and introduction

An extended human presence on the Moon is likely to be beneficial for both scientific and economic reasons (e.g., Spudis, 1996, 2005; Crawford, 2004; Crawford et al., in this issue). It is clear that this aspiration will need to be supported through significant progress in in-situ resource utilisation (ISRU) (e.g., Taylor and Carrier, 1993; Baird et al., 2003; Sen et al., 2005; Anand et al., in this issue). In an effort to prepare for a return to the Moon in the foreseeable future, as well as to enable further space travel to Mars, NASA defined a set of specific targets (NASA, 2007a, 2007b). These include the identification and characterisation of lunar resources; the demonstration of ISRU concepts, technologies and hardware; the use of the Moon for operational experience and mission validation for Mars; the development and evolution of ISRU capabilities to enable lunar exploration; and the use of ISRU for space commercialisation.

The most important goal of ISRU is arguably the generation of oxygen from lunar materials so that human life may be sustained long-term and an oxidant for rocket fuel may become available (e.g., Taylor and Carrier, 1993). Producing oxygen on the Moon,

instead of supplying it from Earth, would give rise to massive cost savings, and NASA specified its initial target as the annual production of 5 t of oxygen by the year 2022. Another key aspect of ISRU is the production of metals from lunar materials so that a lunar infrastructure may be established. It would hence be advantageous to have a process that allows for the production of both oxygen and metal.

The objective of the present article is to summarise and assess the main methods that have been under consideration for the extraction of oxygen from lunar materials. The classical concepts of hydrogen and methane reduction, vapour phase pyrolysis, sulphuric acid treatment, and molten oxide electrolysis are briefly reviewed; and a novel process developed at the University of Cambridge is described in some detail which employs molten salt electrochemistry to win oxygen and metal simultaneously from solid lunar feedstocks.

2. Lunar geology

The surface of the Moon consists of two main geological units. One is the ancient, light-coloured lunar highlands; the other is the darker, lunar mare ('seas') filling the large impact basins located mainly on the nearside. The chemical compositions of the lunar regolith occurring in these units have been derived from soil samples taken in the Luna and Apollo missions as well as from

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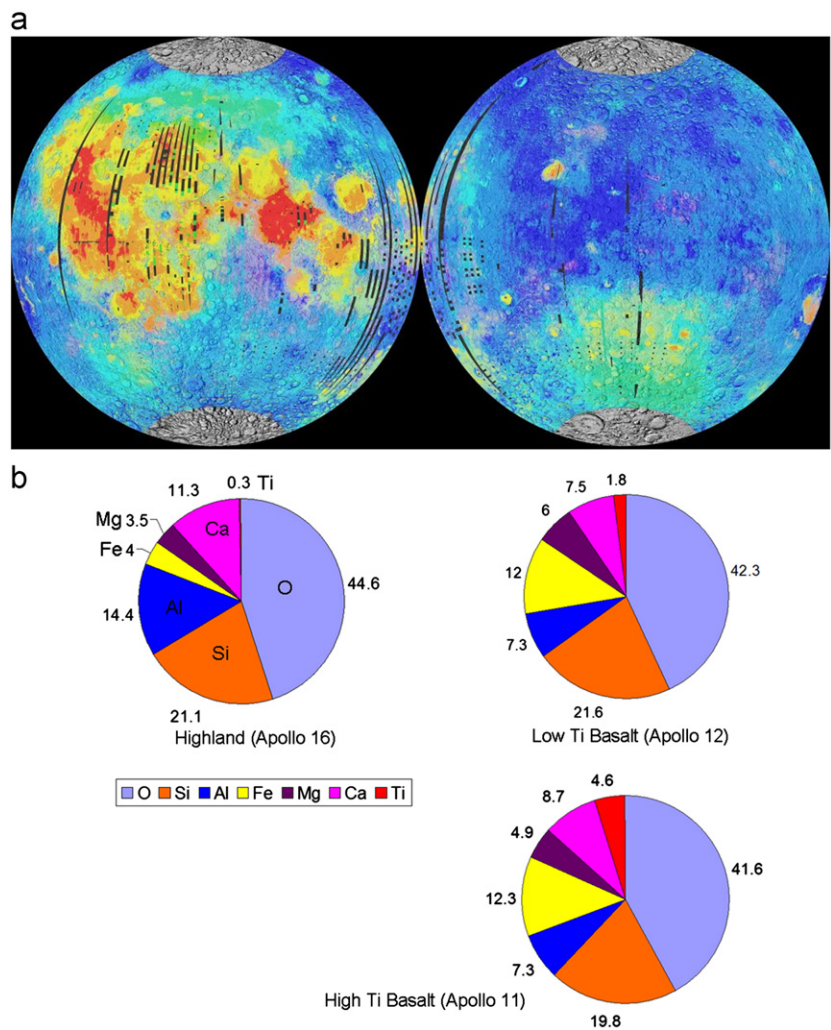


Fig. 1. (a) Distribution of rock types on the nearside (left) and the farside (right) of the Moon. Blue: anorthositic highlands; yellow: low-Ti basalts; red: high-Ti basalts. The large yellow/greenish area in the southern hemisphere of the farside is the South Pole-Aitken Basin, and the colours mostly reflect the more Fe-rich nature of the lower crust exposed by the basin rather than basaltic material (Spudis et al., 2002; image courtesy of Paul Spudis). (b) Chemical compositions of lunar highland minerals (Apollo 16), low-Ti basalts (Apollo 12), and high-Ti basalts (Apollo 11). (Diagrams based on data from Stoesser et al. (2010)).

remote sensing measurements (Heiken et al., 1991; Jolliff et al., 2006). The compositions are summarised in Fig. 1.

The lunar highlands are composed of predominantly anorthositic rocks and contain more than 90% by mass plagioclase in the form of calcium-based anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) and small quantities of magnesium- and iron-bearing minerals such as pyroxene ($(\text{Mg,Ca,Fe})\text{-SiO}_3$) and olivine ($(\text{Mg,Fe})_2\text{SiO}_4$); and the lunar mare is composed of basaltic lava flows which contain varying proportions of plagioclase, pyroxene and olivine as well as ilmenite (FeTiO_3) (e.g., Heiken et al., 1991). Depending on whether the titanium dioxide (TiO_2) content in the basalts is above or below 6% by mass, these are further subdivided into ‘high-Ti’ and ‘low-Ti’ (Neal and Taylor, 1992).

ISRU studies are usually performed with geochemical simulants for lunar regolith. Simulant JSC-1 (NASA, 2005) has a composition approximating that of the lunar mare samples, and the more recent simulant NU LHT (NASA, 2008; Stoesser et al., 2010) has a composition approximating that of the anorthositic highlands. Other factors in the design of lunar simulants are the particle size distribution, the extent of particle agglomeration, and the content of glassy phase. The compositions of the two simulants are given in Table 1.

The south polar highlands in the vicinity of the Shackleton crater are considered to be an ideal location for the return to the Moon. This area provides almost permanent daylight throughout the year,

Table 1
Chemical compositions of lunar simulants JSC-1 (NASA, 2005) and NU LHT (NASA, 2008). Composition ranges are given for JSC-1 to reflect the slightly varying specifications for this material.

Oxide	JSC-1, % by mass	NU LHT, % by mass
SiO ₂	46–49	46.7
Al ₂ O ₃	14.5–15.5	24.4
CaO	10–11	13.6
MgO	8.5–9.5	7.9
Na ₂ O	2.5–3	1.26
K ₂ O	0.75–0.85	0.08
TiO ₂	1–2	0.41
MnO	0.15–0.20	0.07
FeO	3–4	–
Fe ₂ O ₃	7–7.5	4.16
Cr ₂ O ₃	0.02–0.06	–
P ₂ O ₅	0.6–0.7	0.15

which is favourable for both illumination and generation of solar electricity, and will thus facilitate extended periods of residence. The south polar highlands are predominantly of an anorthositic nature (Spudis et al., 2008), and this impacts on the selection of a suitable ISRU process.

3. ISRU processes for the extraction of oxygen from lunar regolith

The extraction of oxygen from lunar regolith may be accomplished by a diverse range of processes. The more classical approaches that have been under consideration for several decades are based on chemical reduction, pyrolysis, acid treatment, or molten regolith electrolysis. A more recent alternative is the reduction of solid regolith through a molten salt electrolytic process. The recent and very exciting discovery of water ice on the Moon may open up the possibility of plain water electrolysis, but the practicality of this notionally straightforward process in a lunar environment warrants a critical assessment.

3.1. Reduction with hydrogen

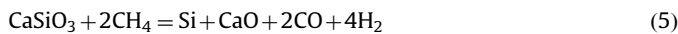
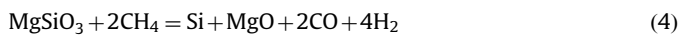
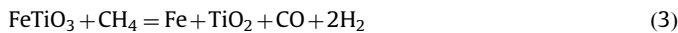
The chemical reduction of lunar feedstock with hydrogen is a conceptually simple approach. The method requires a feedstock such as ilmenite that contains iron oxide, and may be operated at a moderate temperature of around 900 °C (Gibson and Knudsen, 1985; Knudsen and Gibson, 1992; Gibson et al., 1994). The primary product is water, which may be electrolysed to oxygen and hydrogen, with the hydrogen being re-used in further reduction.



The clear disadvantage of the process is that its efficiency depends on the ilmenite content of the feedstock. The process is hence particularly suitable for the lunar mare, and less so for the polar highlands where areas of significant size would need to be mined in order to yield useful amounts of oxygen. A further complication may be the presence of sulphides in the feedstock, as these react to toxic hydrogen sulphide, which would require the addition of a purification step.

3.2. Reduction with methane

The chemical reduction of lunar feedstock with a carbon-based reductant such as methane is applicable to a wider range of materials, because iron oxide and silicon oxide may be reduced, but the method requires a temperature above 1600 °C (Rosenberg et al., 1992, 1996; Gustafson et al., 2006). The primary products are hydrogen and carbon monoxide, with a maximum yield of oxygen of 50%.



It is noted that methane is thermodynamically unstable at the actual operating temperature and decomposes into carbon and hydrogen, with the carbon serving as the actual reductant. The carbon monoxide and hydrogen formed, plus an additional amount of hydrogen, are then converted to methane and water by means of a conventional nickel catalyst. The water is electrolysed, while the methane is re-used.



The disadvantages of the process are its multi-step nature and the high operating temperature in the first step.

3.3. Vapour phase pyrolysis

Vapour phase pyrolysis is another conceptually simple approach. The method may be used with a wide range of lunar

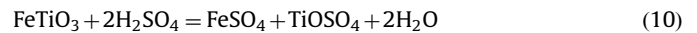
feedstocks, but requires temperatures in excess of 2000 °C to allow at least partial evaporation and decomposition of the metal oxides (Steurer, 1992; Senior, 1993). Most of the oxygen gained stems from the oxides of iron and silicon, while the oxides of magnesium, calcium and aluminium may be decomposed to some extent if temperature and reaction time are sufficient, so that oxygen yields of around 50% are possible. The relevant reaction products appear in the gas phase, which necessitates rapid quenching to preclude back-reactions.



The obvious drawback of the process is its very high operating temperature.

3.4. Sulphuric acid reduction

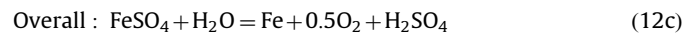
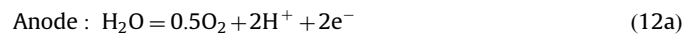
Sulphuric acid treatment may be applied to ilmenite-rich feedstocks (Sullivan, 1992). In the first step the material is reacted with hot concentrated sulphuric acid so that iron sulphate, titanium sulphate and water are formed.



The reaction product is diluted with water and cooled so that the iron sulphate precipitates and can be filtered out. The titanium sulphate hydrolyses and forms titanium dioxide, while part of the sulphuric acid is regenerated.



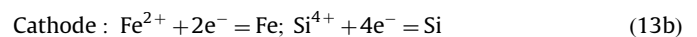
The iron sulphate is then re-dissolved and electrolysed so that iron and oxygen are formed, while the remainder of the sulphuric acid is recovered.



The drawbacks of the process are its complexity and its low oxygen yield for feedstocks of low ilmenite content.

3.5. Electrolysis of molten lunar regolith

The electrolysis of molten lunar regolith is the most straightforward approach of winning oxygen and metal on the Moon (Colson and Haskin, 1992, 1993). This method, termed the Magma process, requires an electrolytic cell, which is operated at temperatures of up to 1600 °C where the regolith is molten, and in which a potential is applied such that oxygen evolves at the anode and metal deposits at the cathode.



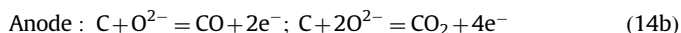
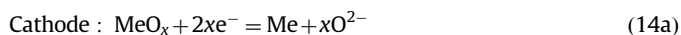
The advantages of the Magma process are that unbeneficiated multi-component lunar feedstock may be employed and that no reagents from Earth are needed. Furthermore, selective winning of metals according to their oxide stabilities is feasible through control of the applied potential (Standish, 2010). Metal products of importance are iron as a construction material and silicon as a raw material for photovoltaic cells. If present in the feedstock, titanium can also be won. The remaining oxides of magnesium, aluminium and calcium are not electrolysed any further. The formation of free magnesium is indeed detrimental, since molten

magnesium may react with the silicon formed at the cathode and thereby degrade its quality, and evaporated magnesium may react with the oxygen in the gas. The overall oxygen yield is around 50%.

The clear disadvantage of the Magma process is its high operating temperature. A key engineering issue is the selection of the anode material, and so far only the expensive platinum group metals (Curreri et al., 2006), and especially iridium (Shchetkovskiy et al., 2010), have shown promise over extended periods of operation. Other drawbacks are: the silicate melt is highly corrosive; the iron in the melt may set up a parasitic current during the early stage of the electrolysis (Sibille et al., 2010); a very viscous spinel of composition MgAl_2O_4 forms towards the end of the electrolysis which is difficult to remove from the apparatus (Standish, 2010).

3.6. Electrolysis of solid lunar regolith

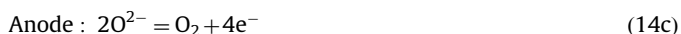
The electrolysis of solid lunar regolith is the latest development in the quest for oxygen extraction processes applicable on the Moon. This approach is derived from the FFC-Cambridge process for the electro-deoxidation of metals and metal oxides (Fray et al., 1999). The FFC process employs an electrolytic cell that is typically operated at temperatures of around 900 °C where the calcium chloride (CaCl_2) electrolyte is molten. In the conventional set-up, a lightly-sintered porous metal oxide body is the cathode and a carbon-based material such as graphite is the anode. The applied potential is sufficiently high to decompose the cathode but also sufficiently low not to decompose the electrolyte. Under these conditions, oxide ions (O^{2-}) are expelled from the cathode into the electrolyte but no calcium metal is deposited onto the cathode (Chen et al., 2000). The calcium chloride electrolyte is able to dissolve oxide ions, and so these ions transport to the anode where they are discharged. At a carbon-based anode, this results in the formation of carbon oxides (CO/CO_2) which are released as a gas. The unique characteristics of the FFC process are that the oxide reduction takes place within the cathode and entirely in the solid state, and that the molten salt electrolyte is not consumed. It is worth mentioning that the FFC process is a generic method which offers numerous applications for the winning of metals and the synthesis of alloys and intermetallics from suitable oxide precursors (Fray, 2001, 2002). The overall reactions for the conversion of metal oxide (MeO_x) to metal (Me) are given below, and a schematic of an FFC cell is presented in Fig. 2.



The electro-deoxidation of titanium dioxide via the FFC process has been the subject of a series of systematic studies. This has provided a very good understanding of the underlying fundamental science, including the precise sequence of reaction steps in the cathode, the transference properties of the electrolyte, and

the reactions at the anode (Schwandt and Fray, 2005; Fray et al., 2006; Alexander et al., 2006, 2011; Schwandt et al., 2009). The scientific results achieved and the practical experience gained were key in the successful production of titanium in pilot plants (Schwandt et al., 2010). This knowledge also formed the basis for the efforts directed at the electro-deoxidation of lunar materials such as ilmenite and regolith.

In its conventional design, the FFC process relies on a carbon-based anode for the discharge of the oxide ions in the electrolyte and their removal from the cell as carbon oxides. In the context of the electro-deoxidation of lunar materials, the desired product is oxygen and, consequently, an anode material is required that is capable of discharging oxide ions and releasing them as molecular oxygen (O_2). The desired anode reaction therefore is the following:



A variety of materials were tested experimentally in an effort to identify an oxygen-evolving anode for the FFC process, but only two showed sufficient promise to be investigated in greater detail. One of these materials was doped tin oxide (SnO_2). This material is commercially available and widely employed as an electrode in silicate glass melts. Plain tin oxide is an insulating and brittle material, but doping with approximately 2% by mass of antimony oxide (Sb_2O_3) and 1% by mass of copper oxide (CuO) renders it electronically conductive and mechanically strong. Doped tin oxide was indeed found to generate molecular oxygen when used as an anode in a melt consisting of calcium chloride and a quantity of dissolved calcium oxide (Kilby et al., 2006; Barnett et al., 2009; Kilby et al., 2010). However, its lifetime was limited to a few hours due to progressive erosion, and its conductivity declined gradually owing to the slow formation of an insulating surface layer of calcium stannate (CaSnO_3). The other appropriate material was the solid solution of calcium titanate and calcium ruthenate ($\text{CaTi}_x\text{Ru}_{1-x}\text{O}_3$) (Fray and Doughty, 2009; Jiao et al., 2009; Jiao and Fray, 2010). Depending on the ratio of ruthenium and titanium, the conductivity of this material ranges from metallic to semi-conducting, and its mechanical strength is sufficient for use in molten salts. It was experimentally proven that this material is able to generate molecular oxygen from calcium chloride melts for more than 100 h without undergoing noticeable erosion or passivation. Therefore, materials of the type $\text{CaTi}_x\text{Ru}_{1-x}\text{O}_3$ are presently the most important inert anode material for the FFC process.

With oxygen-evolving anodes available, studies were conducted on the electro-deoxidation of oxide materials relevant to ISRU. The first series of experiments focused on the electro-deoxidation of ilmenite and, upon successful completion of these, the second series aimed at lunar simulants. In a typical laboratory experiment, the cathode comprised gramme quantities of oxide feed material, the molten salt electrolyte was composed of calcium chloride with minor additions of calcium oxide, and the anode consisted of either doped tin oxide or a calcium titanate/calcium ruthenate mixture. The temperature was around 900 °C, the gas atmosphere was dried argon, the applied potential was around 3 V, and the duration of polarisation was several hours. A schematic of the electrolytic cell is presented in Fig. 2, and a typical laboratory reactor is displayed in Fig. 3.

Quantities recorded during an electro-deoxidation experiment were the current through the electrolytic cell and the oxygen content in the argon gas stream at the reactor outlet. The current was measured by the electrochemical equipment, and the oxygen content was monitored with a commercial lambda-probe. The results obtained in a typical laboratory experiment are presented in Fig. 4. The current is high at the beginning of the experiment, then falls gradually, and finally reaches a plateau. The oxygen content in the argon gas stream follows this trend closely. It is

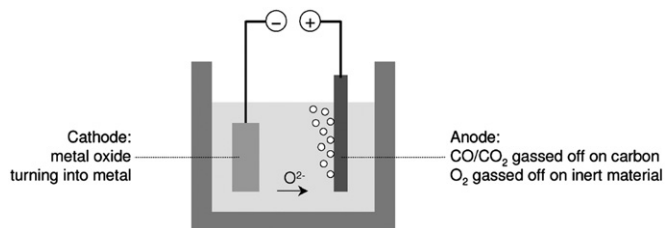


Fig. 2. Schematic FFC cell, indicating oxide-to-metal conversion at the cathode, oxide ion transport through the molten salt electrolyte, and gas evolution at the anode.

clear from Reactions (14a) and (14c) that, during electro-deoxidation, the oxygen from the oxide cathode is expelled into the molten salt electrolyte in the form of oxide ions, and then these ions are transformed into molecular oxygen at the anode and

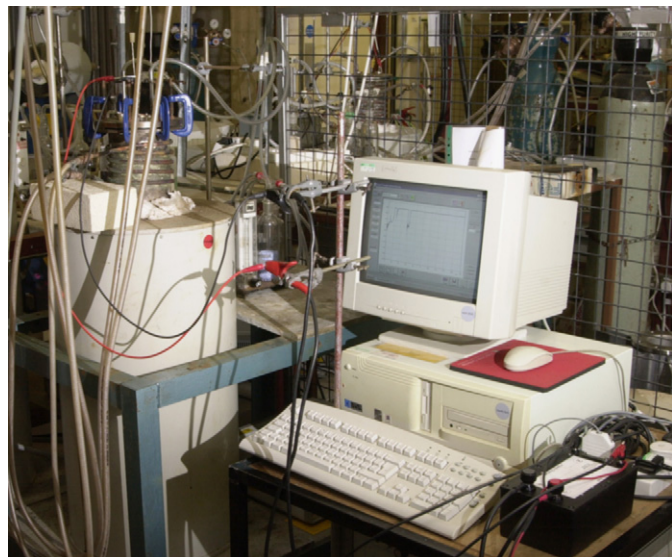


Fig. 3. Laboratory set-up for the electro-deoxidation of lunar materials, consisting of tubular metal retort inside an electrical furnace and electrochemical equipment.

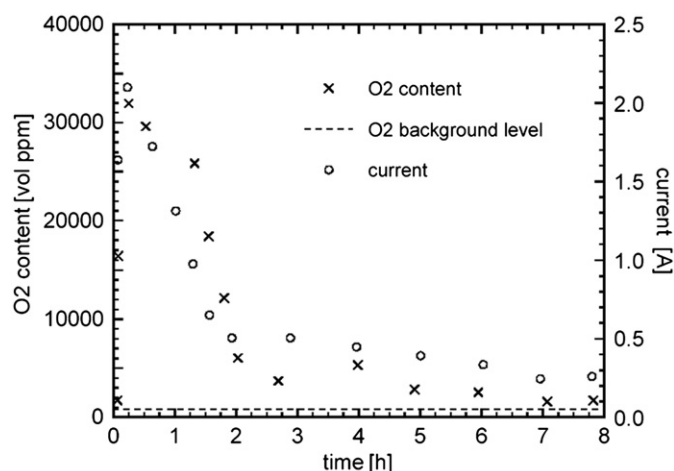


Fig. 4. Curves of current versus time and oxygen gas versus time recorded during a typical electro-deoxidation experiment, using an oxide cathode, a molten calcium chloride electrolyte and an oxygen-evolving anode at a temperature of 900 °C under a flow of argon gas (Kilby, 2008).

released into the argon gas flow. The results in Fig. 4 therefore indicate that the conversion of the oxide to the corresponding metal commences at a high rate and then decelerates as it approaches completion.

Both ilmenite and lunar simulants were electro-deoxidised in the manner described above and the reduction products were subjected to visual and electron microscopic examination. Optical photographs of materials concerning the study on ilmenite are collected in Fig. 5. The ilmenite powder was pressed and sintered into porous oxide tiles, and these were reduced to metal with varying degrees of residual oxygen. Fully reduced metallic material was button-melted into a solid body of iron-titanium alloy. Electron micrographs of materials from the investigation of lunar simulant JSC-1 are shown in Fig. 6. The original JSC-1 powder had a coarse microstructure with oxide particles of varying sizes and irregular shapes. The reduced material was metallic, and the expected presence of calcium, magnesium, aluminium, silicon and iron was verified by elemental analysis. The microstructure of the metallic material was heterogeneous with areas rich in aluminium and silicon and others rich in magnesium and iron. Of course, in both cases, the winning of pure metals from the raw electro-deoxidation product requires a subsequent electro-refining step.

The weaknesses of the electro-deoxidation process in its present form are arguably twofold. Firstly, prior to use, the oxide powder feed material needs to be subjected to a cumbersome pre-treatment involving the pressing of tiles and their sintering into compact oxide bodies. Secondly, due to the porous nature of the solid metal product, a quantity of electrolyte is removed from the cell during harvesting, which then requires replenishment with fresh salt supplied from Earth. It is the objective of ongoing work to eliminate these issues. Specific goals are to modify the electro-deoxidation process in such a way that a powder oxide feed material may be added through a suitable feeding system and that a liquid cathode forms by raising the reactor temperature above the melting point of the alloy product. It is noted that the supply of a powder reactant and the winning of a liquid product are well-known concepts in electro-metallurgy.

3.7. Electrolysis of water

One of the most exciting events in recent lunar research was the apparent detection of significant quantities of water ice on the Moon's surface (see Anand (2010) for a brief review). This discovery was made during NASA's LCROSS mission in 2009, from the analysis of a plume of debris that arose from the impact of an empty Centaur rocket stage onto the interior of a permanently shadowed crater near the lunar south pole (Colaprete et al., 2010). The data recorded suggest that the amount of water in the soil of the crater was approximately $5.6 \pm 2.9\%$ by mass (Colaprete et al., 2010), although this value awaits further confirmation. This would

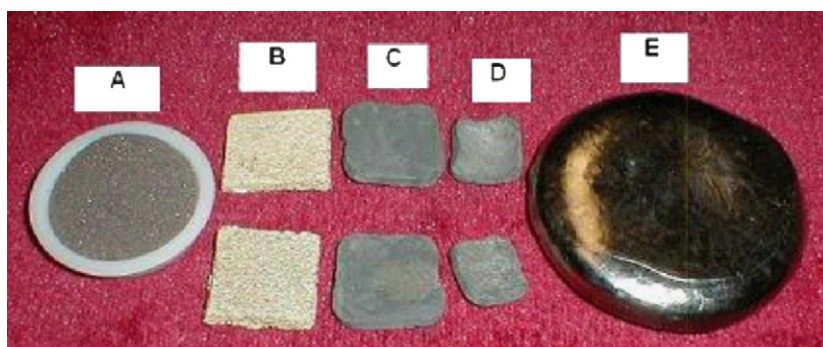


Fig. 5. (A) Original ilmenite powder; (B) pressed and sintered ilmenite tiles; (C) 95% reduced ilmenite tiles; (D) >99% reduced ilmenite tiles; (E) a button-melted iron-titanium alloy body.

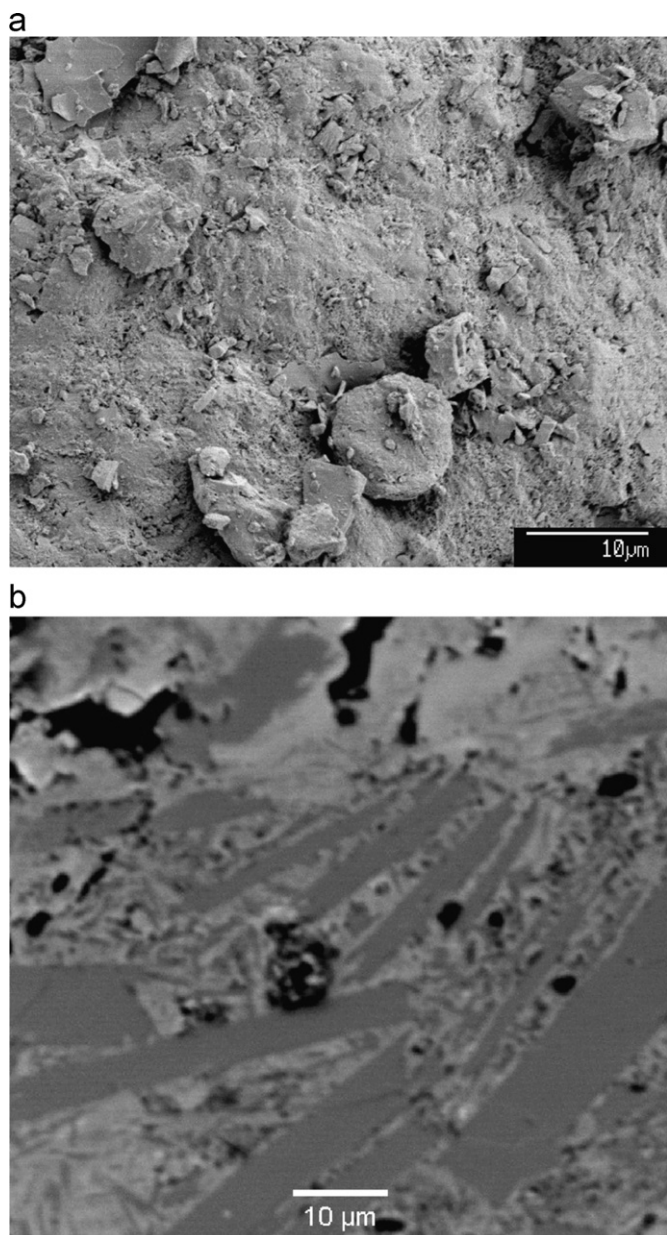


Fig. 6. (a) Electron micrograph of as-supplied lunar simulant JSC-1; (b) electron micrograph of reduced and polished JSC-1; the darker lath-shaped areas are Al and Si rich, the lighter areas are Mg and Fe rich, the black areas are pores.

mean that around 100 l of water could be extracted from one cubic metre of lunar soil.

It is straightforward to assume that the presence of significant quantities of water on the Moon may have a bearing on further ISRU research and development activities, because oxygen could simply be generated from the electrolysis of this water. However, it needs to be considered that the water ice was discovered in a crater experiencing temperatures of around -230°C or less (Paige et al., 2010), which will make its mining and melting very energy-consuming and costly. As the crater is in permanent shadow, the immediate use of solar power is not possible. Consequently, either the ice-bearing soil would need to be transported to the illuminated and warmer parts of the lunar surface, or energy would need to be transported to the ice-bearing sites. It is evident that both these options will be difficult to realise due to the very challenging lunar topography in the south polar highlands. Therefore, the utilisation of the water ice reservoirs on the Moon may prove to

be problematic from an operational standpoint, although of course the scenario might change if the occurrence of sub-surface ice were to be confirmed in areas with occasional exposure to sunlight (Paige et al., 2010). However, many scientifically interesting areas of the Moon are located well away from the polar regions (e.g., Crawford, 2004; Crawford et al., 2007; Flahaut et al., in press), and their exploration would benefit greatly from non-water-based oxygen production methods such as the new process proposed in this article. In addition, using water as a source of oxygen will not simultaneously yield useful metals as a byproduct. Clearly, all these tradeoffs need to be carefully assessed.

3.8. Energy sources

All of the aforementioned processes for the winning of oxygen from lunar materials are reliant on the input of energy, and this is particularly significant for those involving very high processing temperatures. Thus far, solar energy has been considered as the preferred energy source. Solar energy can be exploited through either photovoltaic cells or solar concentrators. The general feasibility of the latter has already been demonstrated which probably renders it the present system of choice (Nakamura et al., 2008; Nakamura and Senior, 2008). Notably, these studies also describe the successful design and utilisation of regolith melting capabilities, which lends further credibility to the feasibility of melt-based electrolysis techniques.

4. Conclusions and outlook

The present article has provided a summary and assessment of the various methods that are under consideration for the extraction of oxygen from lunar materials. Classical approaches are based on chemical reduction with hydrogen or methane, vapour phase pyrolysis, or sulphuric acid treatment. While all these methods have been demonstrated successfully in the laboratory, they also exhibit major drawbacks. A particular issue is that these methods are only able to provide high yields of oxygen when the feedstock is rich in iron oxide. Another classical approach is based on the electrolysis of molten regolith. This does not require a specific feedstock, but the operating temperature is very high and there are a number of processing issues.

The main emphasis of this article has been on a novel electro-deoxidation method that has been derived from the FFC-Cambridge process for the direct molten salt electrolytic conversion of metal oxides into the corresponding metals and alloys. This method relies on the electrolysis of solid oxides in such a way that the oxygen from an oxide cathode is extracted in its ionic form, transported through a molten salt electrolyte, and then liberated in its molecular form at a suitable anode. The method has been validated in the laboratory, and it has the additional advantage that a metal product is generated concurrently with the oxygen. In order for this to become possible, it was necessary to identify a material that may be used long-term as an oxygen-evolving anode in the molten salt electrolyte. This is a key advance that is also of immense importance to the successful industrialisation of the FFC process for terrestrial applications. The utilisation of an oxygen-evolving anode, as opposed to a carbon oxide-evolving one, makes the process environmentally more benign and also precludes a possible deleterious build-up of carbon impurities in the metallic product.

The recent apparent discovery of water ice at the poles of the Moon is clearly of great significance for lunar ISRU, but the mining, melting and electrolysis of the water ice would face tremendous practical challenges owing to its most inconvenient location in extremely cold polar areas. Moreover, many areas of scientific

interest exist at large distances from the poles, the exploration of which would be facilitated by non-water-based oxygen production schemes such as the FCC-Cambridge process proposed here. This process will in addition yield useful metals as a byproduct, which a purely water-based process will not.

A definite assessment of the processes presented for oxygen winning in the lunar environment is a difficult task. Thus, although methods such as hydrogen reduction, methane reduction, vapour phase pyrolysis and sulphuric acid reduction have been known for a long time, it is still desirable to search for novel in-situ resource utilisation techniques. It is anticipated that molten salt-based processes may have a high chance of success because of their inherent advantages in terms of process control and their ability to produce oxygen as well as metal. Overall, the research on, and the development of, alternative ISRU processes for the extraction of oxygen from lunar materials continues to be an area of major relevance for future lunar exploration.

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