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Electrochemical processing using slags, fluxes and salts

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Electrochemical processing using molten electrolytes is undergoing a considerable renaissance due to several innovative ideas being explored both in the laboratory and also at the pilot scale. Several of these new ideas are related to developments in energy generation and storage and involve solid electrolytes. Sodium has been prepared by the electrolysis of sodium carbonate or sodium hydroxide with the transfer of sodium ions through a sodium beta" alumina membrane and magnesium oxide dissociated by the removal of the oxygen through a stabilized zirconia electrolyte incorporating a fuel cell electrode. By using halides with highly electropositive cations, such as molten calcium chloride, it has been found that the favoured cathodic reaction, when oxygen is present, is the ionization of oxygen and not the deposition of calcium. This approach has been applied to the reduction of many metal oxides including titanium, zirconium, niobium and rare earth oxides and, by using a mixture of oxides as the cathode, homogeneous alloys are produced. This concept can also be applied to deoxidation of solid and liquid metals. Refining of metals is possible using intercalation compounds and, in a completely different application, it has been found that, by intercalating alkali metals by electrolysis of alkali halides into graphite, it is possible to produce carbon nanotubes and nanoparticles. The technological opportunities of these various concepts will be discussed.

Introduction

Molten salts and slags have been used for the extraction and refining of metals for centuries. Since the development of large scale electrolysis for the production of light metals, there have been very few radical innovations in the past 100 years until, perhaps, the middle nineteen nineties when several new and very interesting ideas became apparent. Prior to that time, slags, molten salts and fluxes had been used to collect impurities during the refining of metals as in iron and steel making, and refining of copper and aluminium and other non-ferrous metals. In some cases there was an exchange of ions in order to refine the metals, as in the case of addition of aluminium chloride to remove magnesium from aluminium.

The other major application of molten salts is the electrolysis of salts or species dissolved in salts to produce molten metals. In the case of aluminium, the development of the Hall-Heroult process lead to the mass production of aluminium. Prior to this electrolytic route for aluminium extraction, aluminium was little more than a curiosity to make statues and cutlery—artefacts that would rarely be made of aluminium today. It was the conversion to an electrochemical process that led to the immense expansion of the aluminium industry. One interesting question is whether electrochemistry can bring about a similar transformation with other metals? This paper goes some way to answering this intriguing question. Molten salts and slags are also the product of metal reduction processes as in the aluminothermic reduction of chromium oxide the reduction of titanium and zirconium chlorides by magnesium or sodium, or the extraction of tantalum by the reduction of a potassium tantalum fluoride by sodium.

An examination of the decomposition potential of even the most stable, salts such as calcium fluoride, show that it is a fairly modest value indicating that, in theory, processes using electrochemistry should not be energy intensive and should certainly be attractive for many of the more expensive metals. Furthermore, it may be possible to prepare the reductant, such as sodium, by a more economical method than is used at present. As many of reductants are highly reactive with respect to the atmosphere and moisture and are difficult to store, it would be better if the reductant could be produced at the point of use. However, none of these possibilities can be achieved without new ideas involving molten salts and other high temperature phases.

Compared to the metallurgical industry, where research activity has recently stagnated, vast sums of money are being poured into the development of fuel cells and novel batteries to create new methods of energy generation and storage. Some of these processes, such as high temperature oxide fuel cells, carbonate fuel cells and sodium based high temperature batteries, operate at temperatures in the range of interest to the metallurgical industry. It is informative to examine these developments as possible innovative processes for metal extraction, refining and recycling.

Use of solid electrolytes

Probably the two best known solid electrolytes that are commercially available, are stabilized zirconia ($0.15CaO.0.85ZrO_2$), an oxygen ion conductor used in sensors and high temperature fuel cells, and sodium beta"alumina ($Na_2O.5Al_2O_3$), a sodium ion conductor used in high temperature batteries and sensors.

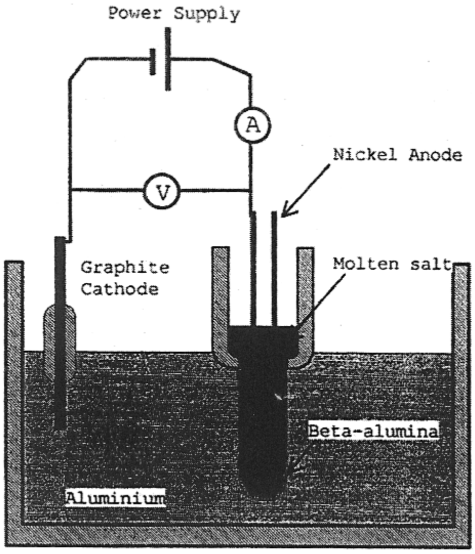

Figure 1. Schematic arrangement for electrochemical addition of sodium to aluminium[3]

Sodium beta"alumina

Metals such as titanium, zirconium, tantalum, hafnium and niobium can be produced in high purity form by reacting their chlorides with sodium[1]. However, at this time only tantalum is produced by sodium reduction of the potassium tantalum fluoride[1]. Additional uses of sodium are in lead refining, for optimizing the properties of aluminium silicon alloys, and improving the properties of bronzes. Sodium is prepared by the electrolysis of molten sodium chloride and it appears to be relatively expensive and, as mentioned above, it is a hazardous material to store.

For some *in situ* applications, it may be possible to electrolyze either sodium chloride or sodium hydroxide to produce sodium and chlorine or sodium, water vapour and oxygen. However, chlorine is also a hazardous material and frequently the metals such as aluminium and lead can react with sodium hydroxide, making *in situ* preparation not particularly attractive. In 1996, it was proposed that a possible method would be to perform the electrolysis of the sodium carbonate or hydroxide inside a sodium beta" alumina tube[2]. The arrangement of the cell is shown in Figure 1 and the majority of the experiments were directed at adding sodium to aluminium-silicon alloys in order to improve the microstructure. The overall cell reactions are:

Anodic $$2OH^- = H_2O_{(g)} + 1/2O_{2(g)} + 2e \qquad [1]$$

Transfer of sodium ions

$$Na^+{}_{(NaOH)} = Na^+{}_{(sodium\ beta\ alumina)} \qquad [2]$$

Cathodic $$2Na^+ + 2e = Na_{(Al-Si)} \qquad [3]$$

The sodium that was produced was also used to reduce metal salts, such as magnesium, from magnesium chloride and zirconium from zirconium chloride[3].

$$2Na_{(1)} + MgCl_{2(1)} = 2NaCl_{(1)} + Mg_{(1)}. \qquad [4]$$

An intriguing alternative is not to discharge the sodium on the surface the beta"alumina but to allow it to diffuse into the molten salt and to discharge the magnesium ions at the cathode. In this case most of the cell reactions are the same except for the cathodic reaction which becomes,

$$Mg^{2+} + 2e = Mg_{(1)} \qquad [5]$$

The overall cell reaction is:

$$NaOH + MgCl_2 + 2e = 2NaCl + Mg + H_2O_{(g)} + 1/20_{2(g)} \qquad [6]$$

If sodium carbonate is used instead of sodium hydroxide, the reaction is:

$$NaCO_3 + MgCl_2 + 2e = 2NaCl + Mg + CO_{2(g)} + 1/20_{2(g)} \qquad [7]$$

The decomposition potentials for these reactions are well below 2V and if the evolved gases are allowed to react with carbon,

$$3C + H_2O + 1/2O_2 = 3CO + H_2 \qquad [8]$$

or

$$2C + CO_2 + 1/2O_2 = 3CO \qquad [9]$$

the decomposition potentials are well below 1 V. The inputs are magnesium chloride, sodium carbonate or sodium hydroxide and carbon; the products are sodium chloride, magnesium and reducing gases.

Zirconium and titanium can also be prepared by these routes, but in these cases the products are either finely divided metal powders or dendritic deposits on the cathode, depending on whether the sodium or the metal is discharged [4].

As well as adding sodium to molten metals by this approach, it is also possible to remove sodium, a contaminant found in the aluminium produced in the Hall-Heroult process[5].

Stabilized zirconia

For many years research workers have considered using stabilized zirconia as an oxygen conducting membrane to remove oxygen from molten metals, especially copper[6,7]. The overall reaction is

$$O_{(Cu)} + 2e = O^{2-}{}_{(stabilized\ zirconia)} \qquad [10]$$

$$O^{2-}{}_{(Stabilized\ \ zirconia)} = 1/2O_2 + 2e \qquad [11]$$

The emf for this reaction can be further reduced by reacting the oxygen with a reducing gas, for example, hydrogen

$$O^{2-}{}_{(Stabilized\ \ zirconia)} + H_2 = H_2O + 2e \qquad [12]$$

Consideration has also been given to allowing the oxygen ions in the cryolite melt to pass through a stabilized zirconia and to react with a reducing gas[8]. However, there are problems with the stability of the stabilized zirconia in such an aggressive melt.

Pal and coworkers have extended this concept to the reduction of other metal oxides by dissolving the oxide in a molten salt, plating out the metal, and transferring the oxygen ions through the solid electrolyte membrane where they react with hydrogen[9]. A schematic of their cell is shown in Figure 2. Magnesium oxide was dissolved in neodymium chloride salt and on the application of a

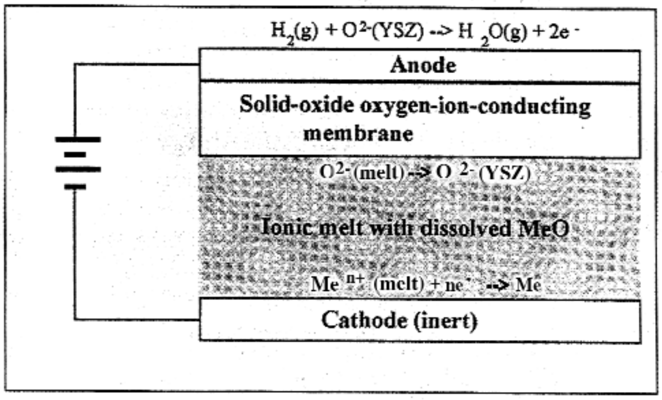

Figure 2. The SOM process for metal (Me) extraction by direct reduction of its oxide[9]

potential magnesium droplets were produced on the cathode and water vapour was formed by the reaction of the oxygen with water vapour on the external face of the stabilized zirconia.

Recently, these authors have been investigating the reduction of tantalum oxide by this technique. However, in this case, the tantalum would be deposited as a solid, unlike magnesium, and the deposit is likely to be highly dendritic as it has proved virtually impossible to plate out coherent solid plates of metals from molten salts. A further disadvantage of this process is that in order to have a high ionic conductivity in the stabilized zirconia, the temperature has to be in the range of 1500 to1700 K but this problem could be overcome by using a solid oxygen conductor that has a reasonable conductivity at much lower temperatures such as $Ce_{0.8}Gd_{0.2}O_{1.9}$[10].

Oxygen ion conducting liquid electrolytes

Any molten salt or slag containing oxide should, in theory, conduct oxygen ions but frequently this ionic conduction is swamped by the electronic contribution of the multivalent ions, such as Fe^{2+} and Fe^{3+}, in solution. In order for the melt to be ionic, it is important that the melt consists of compounds that are strongly ionic such as the oxides and halides of the alkali and alkaline earth metal.

By far the most successful oxygen ion containing electrolyte is alumina dissolved in cryolite, Na_3AlF_6, which allows the production of about 22m tonnes of aluminium per annum. Unfortunately, it has not proved possible to extract other metals by a similar route as few metal oxides are soluble in salts. As many metals melt at greater temperatures than the volatilization temperature of the salts, the metals are cathodically deposited in a very dendritic form at commercial current densities.

Attempts have been made to reduce titanium dioxide to titanium in a slag both below and above the melting point of titanium[11]. In the case of a solid titanium product, as well as the dendritic problems alluded to above, it was found that the product also had considerable quantities of oxygen due to the equilibrium between the oxygen containing melt and the metal. It should be noted that titanium and a few other reactive metals have substantial solubility for oxygen in the solid state and this is very detrimental to the physical properties of the metals.

Electro-deoxidation

An alternative approach has been investigated at the University of Cambridge where, instead of attempting to find electrolytes for specific metallic oxides, the oxide is made the cathode in a bath of a salt of a strongly electropositive element. This salt should also have some solubility for its own oxide. The solubility of most oxides in their halides is relatively low but the oxides of calcium, strontium, barium and lithium all have substantial solubility.

From a possible commercial viewpoint, calcium chloride is very attractive—it is a waste product of the chemical industry and is relatively cheap, has a very high solubility in water and has the same toxicity as common salt so that disposal problems should not be severe. In 2000, it was found that it was possible to reduce titanium dioxide directly to the metal by the process of electro-deoxidation in a calcium chloride melt[12]. The preferred cathodic reaction was the ionization of the oxygen from the oxide

$$O_{(TiO_2)} + 2e = 0^{2-}{}_{(calcium\ chloride)} \qquad [13]$$

rather than the discharge of the calcium cation and deposition of calcium

$$Ca^{2+} + 2e = Ca \qquad [14]$$

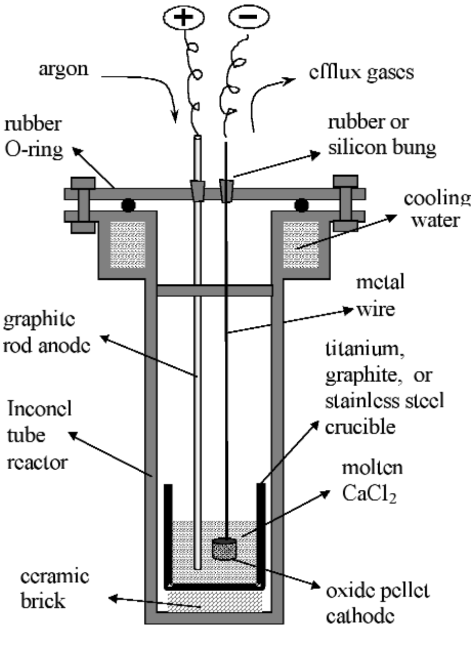

Figure 3. A schematic diagram of the laboratory electrolytic cell used for demonstrating the proposed electro-deoxidation[12]

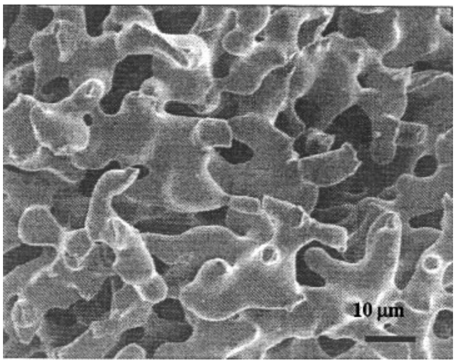

Figure 4. The microstructure of the as-produced titanium obtained from electro-deoxidation of TiO_2 in molten $CaCl_2$[12]

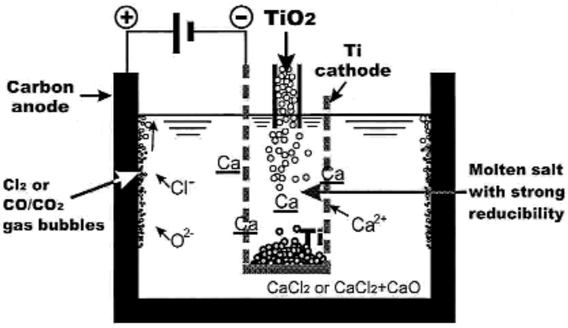

Figure 5. A schematic diagram showing the concept of combining electro-winning of calcium, calciothermic reduction and, inevitably, electro-deoxidation for the reduction of TiO_2 to Ti metal[19]

A schematic of the cell is shown in Figure 3. Extensive cyclic voltammetry measurements demonstrated that on increasing the cathodic potential, the first reaction that took place was the interaction between the calcium chloride and the oxide, either to form an intercalation compound or a calcium titanate[13].

Further increases in the cathodic potential resulted in oxygen ionization and finally deposition of calcium as calcium metal. From the cyclic voltammetry curves it is apparent that even if a high voltage is applied across the cell, electrodeoxidation will always take place after the formation of the intermediate compounds as this reaction is more energetically favourable than the calcium deposition reaction. It should be noted that due to the relatively high solubility of calcium in molten calcium chloride, some reactions involving calcium can take place below the accepted decomposition potential of the electrolyte.

In the case of the reduction of titanium dioxide, the product consisted of nodules of titanium, as shown in Figure 4, not dissimilar to Kroll sponge formed by the reduction of $TiCl_4$ by molten magnesium. This work has been repeated at other laboratories and, depending upon the time of electrolysis, it was possible to reduce the residual oxygen content to below 60 ppm[14].

It is obvious that this approach is not restricted to titanium, but can be applied to the majority of the oxides of the metals found in the periodic table. In the laboratory, the oxides of niobium, zirconium, tantalum, tin, chromium, manganese, uranium, hafnium, silica have been reduced. In each case, using porous pellets, it was found that the electro-deoxidation reaction took several hours, but the amount of time required was reduced when there was no solubility of the oxygen in the metal as in the case of chromium[15]. Other workers have studied the reduction of uranium dioxide[16] and silica[17]. This method compares favourably with the existing processes that can take a few weeks, as in the case of titanium and zirconium.

During the electro-deoxidation reaction, the only species that are removed are the anion species, which means that the cationic elements report as metals in the final product. This can be a disadvantage if the feed material is impure and refining is required. However, this lack of refining can be used to considerable advantage if alloying is required.

At the present time, it is very difficult, if not impossible, to produce alloys directly by electrolyzing a mixture of molten salts as the deposition potentials of the various metallic elements vary quite considerably and, unlike aqueous solutions where it is possible to complex ions to bring the deposition potentials closer together. Complexes in molten salts are usually not very stable and can only alter the decomposition potentials by a few mV rather than the 100 mV that are required to bring the deposition potentials closer together. The only way an alloy can be produced is to ensure that the deposition rate of the more noble element is controlled by mass transfer, but this is very much influenced by the convective conditions within the melt.

It was found that simply by mixing the oxides together and applying the electro-deoxidation technique, homogeneous alloys and intermetallic compounds could be formed. These included TiAl, Ni Ti, NbTi, Nb_3Sn, Mo_2Si and SiC [18].

Calcium deposition from ionic melts

An alternative process is being developed in Japan by Ono and Suzuki where calcium is used as a reductant to reduce titanium dioxide[19]. In one mode, the calcium is prepared in an external reactor by the electrolysis of calcium chloride or a solution of calcium oxide in calcium chloride. Then the solution of calcium in the electrolyte is transferred to a reactor where the reduction of the titanium dioxide takes place, forming calcium oxide, which dissolves in the electrolyte, and can be returned to the electrowinning reactor.

In a later version of the process, Figure 5, the two reactors are combined so that electrowinning of the calcium and the reduction of the titanium oxide granules takes place simultaneously. As the rate of reaction of the titanium dioxide is much greater when the granules are held close to the cathode, it may be that electro-deoxidation may also be taking place. One problem is that in the presence of considerable quantities of calcium in the electrolyte is that the electronic conductivity can become significant, and this essentially short circuits the ionic current and makes the current efficiency for the whole process very low[20].

Okabe *et al.* have used a variation of this process where they used calcium vapour to reduce titanium dioxide[21]. It is well known that this reduction process is thermodynamically possible but usually there are problems in removing the calcium oxide product. Okabe *et al.* avoided this problem by incorporating calcium chloride into the titanium dioxide so that advantage could be taken of the property of molten calcium chloride to dissolve considerable quantities of calcium oxide. As the calcium oxide dissolves at a reduced activity, the driving force for the reduction reaction is also increased. Furthermore, the calcium chloride-calcium oxide mixture readily dissolves in water or dilute acid.

Electro-deoxidation of molten metals

Earlier in this paper the removal of oxygen from molten copper using a solid electrolyte was described. This is always likely to be a slow process due to the limited surface area presented between the oxide conductor and the melt and the relatively low ionic conductivity of the solid electrolyte. Calcium chloride and its solutions have relatively high ionic conductivities and, as has been seen, very effective at removing oxygen from oxides and solutions of oxygen in solid metals.

However, the problem of increasing the surface area of contact between the salt phase and the metal to be refined has to be addressed. This was overcome by using a recessed electrode in which the molten metal is allowed to flow down the surface of electrode in the form of droplets and rivulets. This greatly increases the surface area of the reactive surface, Figure 6[22]. Various experiments were performed where a cathodic potential was applied. It was found possible to reduce the oxygen down to very low

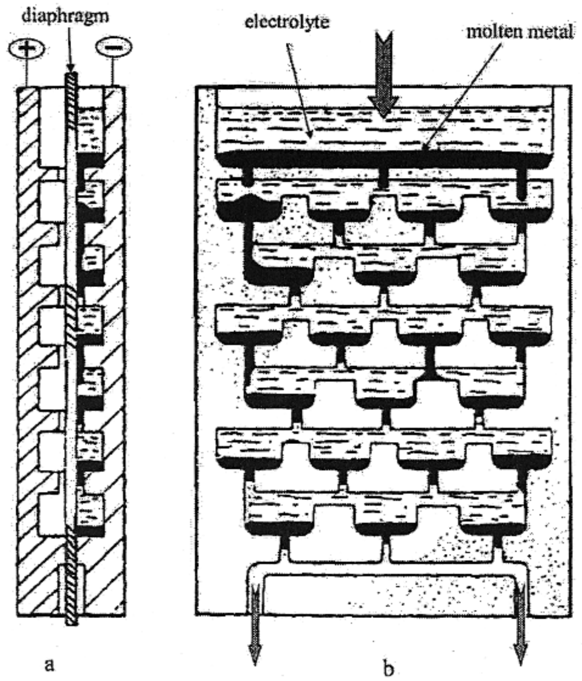

Figure 6. Schematic diagrams of (a) the recessed channel electrode assembly and (b) details of the recessed channels in the electrode surface[22]

values, as is shown in Table 1. It is interesting to observe that the sulphur and selenium were also removed at the same time, which is another advantage over the solid electrolyte approach where only the oxygen was removed.

Electro-refining of metals

So far in this paper only cathodic reactions have been considered but, as is well known, it is possible to electrorefine metals in molten salt baths. However, fused salt electrorefining has never been used except for the refining of aluminium to create high value-added products for the electronics industry. The reason for this is not the electrochemistry, as electrorefining only requires a few mV to ionize an element from the anode and discharge it at the cathode, but the design of the cells that cause large IR drops to occur in the cell.

A further problem at high current densities is that the element that is being ionized cannot diffuse fast enough to the anode/molten salt interface to satisfy the applied current, so that the element which is next in the electrode potential series will ionize and eventually discharge at the cathode causing contamination of the cathode product. This can be prevented by stirring the anode, but in many cells this is not easily achieved without disrupting the anode pool/molten salt interface, causing droplets to migrate to the cathode and causing contamination.

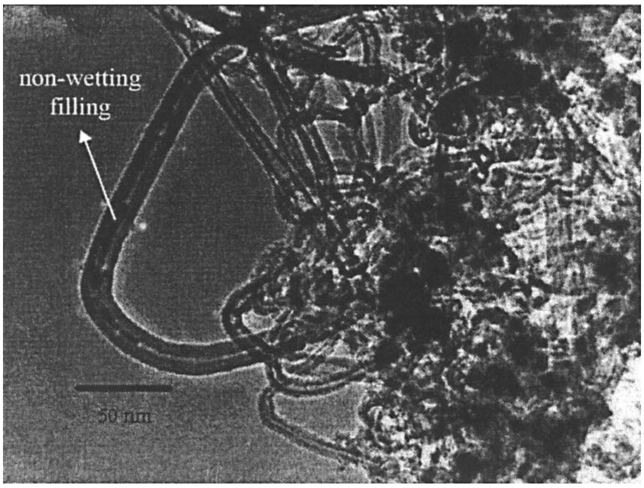

Figure 7. A TEM image showing the carbon nanotubes produced by electrolysis of a graphic cathode in molten LiCl[29,30]

The recessed electrode cell in which there are two recessed graphite plates separated by a diaphragm, all immersed in the molten salt electrolyte is shown in Figure 6. When the molten metal flows down the anode plate, as well as increasing the surface area, conditions for very high mass transfer are created. As the anode to cathode distance is very small, a matter of mm, the IR drop in the electrolyte is negligible so that the overall potential drop can be as low as 100 mV[23]. Furthermore, as the potential drop is so small, the cell potential can be controlled so that only one species ionizes. This cell has been applied to the refining of lead zinc[23], lead bismuth[24] and aluminium magnesium alloys[25].

Intercalation from molten salts

Intercalation is a process where an ion or an atom is inserted into the planes of a compound, such as lithium in cobalt oxide or graphite, and this process forms the basis of the Li-ion battery. One of the properties of the intercalated species is that the diffusion coefficient is very high, which is somewhat surprising given the stability of intercalated compounds. This effect can be used to remove impurities from molten metals by simply setting up a circuit between the intercalating compound, lithium titanate, and the metal through a molten salt electrolyte[26]. This has been used to remove alkali metals from molten aluminium. The USBM were also looking at the removal of other elements, such as magnesium[27].

It has been known for decades that alkali atoms can intercalate into graphite, but recently it was found that by forcing the alkali atoms into the graphite, it is possible to form carbon nanotubes, Figure 7[28-30]. Studies have shown that it appears that the alkali atom goes into the structure and forces out the graphite, either as tubes or as graphite

Table 1. Elemental analysis of the copper sample from IMI Refiner Ltd before and after electrolysis at 1160°C for 2.0h

	As-received	Electrolyzed at 2.6 V in $BaCl_2$	Electrolyzed at 2.6 V in $CaCl_2$	Electrolyzed at 2.1 V in $CaCl_2$	Electrolyzed at 2.1 V in $CaCl_2$
Oxygen/ppm	5500	30	100	50	100
Sulphur/ppm	10	Undetectable	Undetectable	Undetectable	Undetectable
Selenium/ppm	25	Undetectable	Undetectable	Undetectable	Undetectable

sheets that quickly coil to form nanotubes[31-33]. Economically, this seems a cost-effective method of making nanotubes.

Conclusions

This paper has drawn attention to some of the innovative research that is on going to improve extraction processes and to make novel materials. Much of the inspiration for this work has come from the field of electrochemical energy storage and generation. Many of these processes are still at the laboratory scale and it will take time, dedication and resources to make these processes a commercial reality.

However, with the pressures of sustainability and global warming, several of these processes appear attractive. For example, with an inert anode, the electro-deoxidation process can take a metal oxide and convert it directly into metal and oxygen and, provided the electricity came from a renewable resource, this should be a more attractive route than existing processes.

It may be that the application of some of the novel electrochemical technologies, described in this paper, will lead to cheaper and more efficient processes than existing thermal methods. This will expand the market for some of the metals, which are plentiful in the earth's crust but very expensive to produce at the present time. Titanium is such a metal that is very common but expensive and tedious to extract. Will electrochemistry do the same for titanium as it did for aluminium at the start of the last century?

References.

1. *Handbook of Extractive Metallurgy*. HABASHI, F. (ED) Wiley-VCH, Weinheim 1997.
2. DOUGHTY, G., FRAY, D.J., VAN DER POORTEN, C. and DEKEYSER, J. *Solid State Ionics*. Vol. 86-88, 1996. pp. 193–196.
3. DOUGHTY, G.R. and FRAY, D.J. *Ionics* vols. 5&6, 1997. pp. 338–344.
4. DOUGHTY, G.R. and FRAY, D.J. *Molten Salt Forum* vols. 5–6, 1998. pp. 315–318.
5. DOUGHTY, G.R. and FRAY, D.J. *Trans IMM*. vol. 108C 1999. pp. 167–168
6. ODLE, R.R. and RAPP, R.A., Electrochemical studies and processes involving oxygen in liquid metals. *Molten Salts*. Pemsler, J.P., Braustein, J., Morris, D.R., Nobe, K. and Richards, N.E. (Eds.) The Electrochemical Society, Pennington, 1976. p. 622.
7. SORAL, P., PAL, U., LARSON H.R. *et al. Metall Mater Trans B* vol. 30 , 1999. pp. 307–321 no 2.
8. RAPP, R.A. Private communication
9. PAL, U.B., WOOLLEY, D.E. and KENNEY, G.B. *JOM* vol. 53 2001. pp. 32–35 no 10.
10. STEELE, B.C.H. Isotopic oxygen exchange and selection of materials for ceramic ion transport membranes. *High Temperature Materials Chemistry*. Steele, B.C.H. (Ed.) The Institute of Materials, London 1995. p. 49.
11. LARSON, H.R. and EAGAR, T.W. *JOM* vol. 50, 1998. pp. 56–57. no 5.
12. CHEN, G.Z., FRAY D.J. and FARTHING T.W. *Nature* vol. 407, 2000. pp. 361–364.
13. CHEN, G.Z. and FRAY, D.J. *Journal of The Electrochemical Society*, vol. 149, 2002. pp no. 11 E455–E467.
14. WARD-CLOSE, M. GODFREY, A.Private communication.
15. CHEN, G.Z, GORDO, E and FRAY, D.J. In press, *Trans Met B.*
16. GOURISHANKAR, K., REDEY, L. and WILLIAMSON, M. Electrochemical Reduction of Metal Oxides in Molten Salts. *Light Metals 2002*. Schneider, W.A. (Ed.) TMS, Warrendale, Pennsylvania. 2002. p. 1075.
17. NOHIRA, T., YASUDA, K., and ITO, Y. *Nature Materials* vol. 2,2003. p. 397.
18. CHEN, G.Z. and FRAY, D.J. The use of electro-deoxidation to reduce titanium dioxide and other metal oxides. *Proc of the 4th International Conference on Materials Engineering and Resources* (Akita, Japan,) 2001. pp. 1–6.
19. SUZUKI, R., ONO, K. OS Process – Thermochemical approach to reduce titanium dioxide in molten $CaCl_2$. *Yazawa International Symposium – Metallurgical and Materials Processing; Principles and Technologies. Volume III: Aqueous and Electrochemcial Processing*. Kongoli,F., Itagaki, K., Yamauchi, C., Sohn, H.Y. (Eds.) TMS, Warrendale , Pennsylvania. 2003. p. 187.
20. SUZUKI, *R. Ti-2003 10th World Conference on Titanium* Hamburg, Germany 2003.
21. OKABE, T.H., ODA, T., MITSUDA , Y. *Ti-2003 10th World Conference on Titanium* Hamburg, Germany 2003.
22. CHEN, G.Z. and FRAY, D.J. J. *Applied Electrochemistry* vol. 31. 2001. pp. 155–64.
23. DRISCOLL, K.J. and FRAY, D.J. *Trans IMM*, vol. 102, 1993. pp. C109–117.
24. TAILOKA, F. and FRAY, D.J. *Trans IMM*. 1995. vol. 104, pp. C51–58.
25. COX, A., OH, Y. and FRAY, D.J. The potential for electrorefining of aluminium scrap using a recessed channel cell in *5th European Symposium in Electrochemical Engineering*, A.A. Wragg. (ed.) Institution of Chemical Engineers, Rugby 1999. pp. 71–80.
26. HARDEMAN, R.W. and FRAY, D.J. *Materials Science and Tech*. vol. 4, 1988. p. 745.
27. RILEY, W.D. and JONG, B.W. Chloride–free processing of aluminium scrap to recover by-product materials. *Third International Symposium on Recycling of Metals and Engineered Materials*. Queneau, P.B. and Peterson, R.D. (Eds) TMS Warrendale, PA 1995. p. 47.
28. HSU, W.K., TERRONES, M., HARE, J.P., TERRONES, H., KROTO, H.W. and WALTON, D.R.M. *Chem. Phys. Lett* vol. 262. 1996. p. 161.
29. CHEN, G.Z., KINLOCH, I., SHAFFER, M.S.P., FRAY, D.J and WINDLE, A.H. *High Temperature Material Processes*, vol. 2. 1998. pp. 459–469.
30. CHEN, G.Z., KINLOCH, I., SHAFFER, M.S.P., FRAY, D.J and A.H. WINDLE. Electrochemical investigation of the formation of carbon nanotubes in molten salts in *Advances in Molten Salts*, M Gaune-Escard (Ed) begell house, inc. New York 1999. pp. 97–107.
31. XU, Q., SCHWANDT, C., CHEN, G.Z. and FRAY, D.J. *Journal of Electroanalytical Chemistry* vol. 530, 2002. pp. 16–22.
32. DIMITROV, A.T., CHEN, G.Z., KINLOCH, I.A. and FRAY, D.J. *Electrochimica Acta* vol. 48, 2002. pp. 91–102.
33. BORISENKO, N, SYTCHEV, J. and KAPTAY, G. J. *Min. Met* vol. 39, 2003. p. 369.