

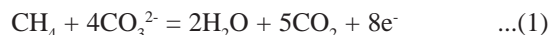
**RENEWABLE ENERGY AND THE ROLE OF MOLTEN SALTS AND CARBON****D.J. Fray<sup>a</sup>**<sup>a</sup> *Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, UK**(Received 20 December 2012; accepted 01 June 2013)***Abstract**

Molten carbonate fuel cells have been under development for a number of years and reliable units are successfully working at 250kW scale and demonstration units have produced up to 2 MW. Although these cells cannot be considered as renewable as the fuel, hydrogen or carbon monoxide is consumed and not regenerated, the excellent reliability of such a cell can act as a stimulus to innovative development of similar cells with different outcomes. Molten salt electrolytes based upon LiCl – Li<sub>2</sub>O can be used to convert carbon dioxide, either drawn from the output of a conventional thermal power station or from the atmosphere, to carbon monoxide or carbon. Recently, dimensionally stable anodes have been developed for molten salt electrolytes, based upon alkali or alkaline ruthenates which are highly electronically conducting and these may allow the concept of high temperature batteries to be developed in which an alkali or alkaline earth element reacts with air to form oxides when the battery is discharging and the oxide decomposes when the battery is being recharged. Batteries using these concepts may be based upon the Hall-Heroult cell, which is used worldwide for the production of aluminium on an industrial scale, and could be used for load levelling. Lithium ion batteries are, at present, the preferred energy source for cars in 2050 as there are sufficient lithium reserves to satisfy the world's energy needs for this particular application. Graphite is used in lithium ion batteries as the anode but the capacity is relatively low. Silicon and tin have much higher capacities and the use of these materials, encapsulated in carbon nanotubes and nanoparticles will be described. This paper will review these interesting developments and demonstrate that a combination of carbon and molten salts can offer novel ways of storing energy and converting carbon dioxide into useful products.

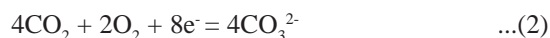
**Key words:** Fuel cells; High temperature batteries; Lithium ion batteries.

**1. Carbonate fuel cells**

Carbonate fuel cells, based upon alkali carbonate melts have been one of the more successful developments in fuel cells avoiding expensive catalysts and problems with interfaces between solid electrolytes and solid electrodes [1]. In a carbonate fuel cell, the fuel which could be hydrogen, carbon monoxide or a hydrocarbon reacts with the carbonate ion to form carbon dioxide at a nickel chromium anode:



At the lithiated nickel oxide cathode, oxygen, from the air, reacts with the carbon dioxide, cycled from the anode, to regenerate the carbonate ion:



The overall reaction using methane is:



The electrolyte is usually a eutectic mixture of Li<sub>2</sub>CO<sub>3</sub> – K<sub>2</sub>CO<sub>3</sub> held in an acicular mixture of lithium aluminate. Typically, the fuel cell generates a

potential of 0.7V at a current density of 0.3A/cm<sup>2</sup> and a substantial number of fuel cell stacks have run for years.

**2. Regeneration of carbon monoxide from carbon dioxide**

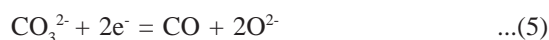
Although the use of electricity from renewable resources, wind, sea, solar is one of the world's goals, a major problem still remains to be solved and that the intermittent nature of the source and the difficulty of storing electricity on a major scale or its conversion into another energy rich material. Recently, the group of Lubomirsky have developed an interesting cell for the conversion of carbon dioxide from power station gases to carbon monoxide [2]. In this case, the electrolyte is a molten mixture of lithium carbonate and lithium oxide. On exposure of the melt to carbon dioxide, the carbon dioxide reacts with the oxide ions to form more carbonate ions.



When a voltage is applied across the lithium carbonate – lithium oxide electrolyte, at temperatures

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greater than 1000 K, the carbonate ion at a titanium cathode is reduced to carbon monoxide:



At a graphite anode, the oxygen ions discharge as oxygen:



In this way, energy from a renewable source could be used to convert carbon dioxide into carbon monoxide which could be readily stored, as it has been for decades, and either used in power stations or converted into valuable chemicals.

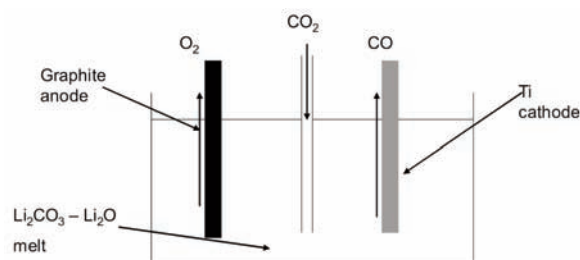


Figure 1. Schematic of cell used to convert carbon dioxide to oxygen and carbon monoxide

More recently, Xu et al. have used a similar technique to deposit carbon, also onto a titanium based cathode but at lower temperature where the deposition of carbon is the thermodynamically favoured reaction over the evolution of carbon monoxide [3]. Although the results of Lubomirsky show that only oxygen is evolved at the carbon anode, thermodynamically it is possible that carbon monoxide or carbon dioxide may form which may consume the anode. An inert anode may be preferable and, recently, inert anodes which stable in chloride oxide melts have been developed and these are based upon the use of titanates, which are mainly insulators, being doped with a few percent of a ruthenate which is highly electronically conducting. It was found that calcium titanate was stable in calcium chloride melts in contact with titanium dioxide [4] but, unfortunately, attempts using doping with compounds containing cations with a different valency to titanium were only moderately successful [5]. However, calcium ruthenate is an excellent electronic conductor [6] and results at low temperature have shown that conducting solid solutions can be made between calcium ruthenate and calcium titanate [7,8]. At high concentrations of calcium titanate these solid solutions are semiconductors with a low electronic conductivity at around 10 K. One of the properties of semiconductors is that the electronic conductivity increases with increase in temperature and it was found that at 1000 K, 10mol% calcium ruthenate in calcium titanate was an excellent conducting inert anode material in calcium chloride-calcium titanate

melts [4].

Given that carbonate fuel cells have been engineered on a significant scale, it should be possible to adapt them to convert carbon dioxide to carbon monoxide, either for use as a fuel or a precursor to many chemical compounds. To convert carbonate fuel cells to the production of carbon is more problematic as a method of removing the deposited carbon would be required.

### 3. High temperature batteries

Decades ago, there was considerable interest in high temperature batteries of the type:

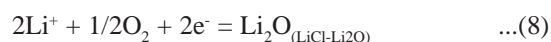


where X is a metal such as tin or zinc [9]. The cells consisted of a layer of lithium floating on molten lithium chloride which in turn floats on the lithium metal and the cell functioned by the lithium ionising, the lithium ions diffusing through the molten salt phase to the liquid-metal alloy, where the lithium ion was discharged. The battery could simply be recharged by applying a reverse current. The advantages of this type of battery were that the all the phases were molten so that the phases would always remain in contact, the molten salt had a very high ionic conductivity and a high rate of mass transfer. Offsetting these advantages is the low thermodynamic potential of the battery of about 0.5 V and, when fully charged, the battery undergoes self-discharge as lithium metal dissolved in the salt and formed a partially electronically conducting electrolyte which essentially acted as a short circuit. With the development of suitable electronically conducting ceramic materials, mentioned above, that can survive in molten salts, these disadvantages can be overcome. One can imagine a cell consisting of a metal lithium anode separated from the inert anode by a LiCl-Li<sub>2</sub>O melt. The reactions of the cell would be:

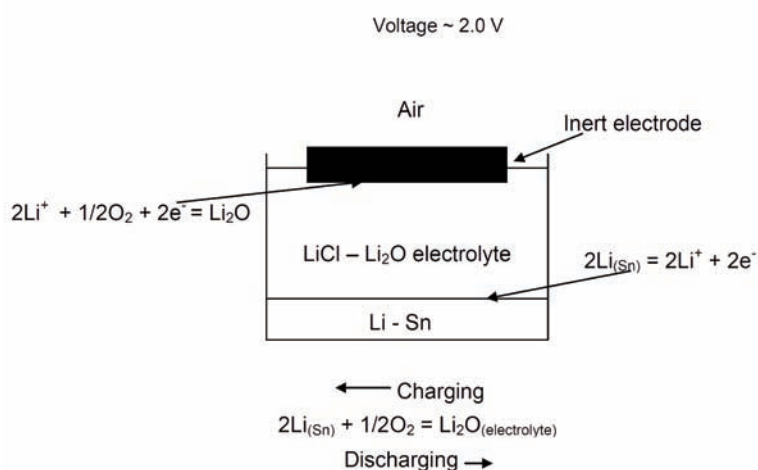
at the lithium alloy anode



and, at the electronically conducting ceramic cathode



The voltage generated by such a cell would be of the order of 2.0V and the battery could be recharged by simply applying a reverse current. When fully charged, the discharge reaction can be prevented by excluding the source of air and removing the inert electrode from the salt. A greater voltage ~ 2.4 V and capacity can be obtained using a CaCl<sub>2</sub>-CaO melt and a calcium tin alloy. These ideas may link to the thoughts of Sadoway of using very large batteries rather like Hall Heroult cells to store energy [10].



**Figure 2.** Schematic of high temperature lithium-air battery

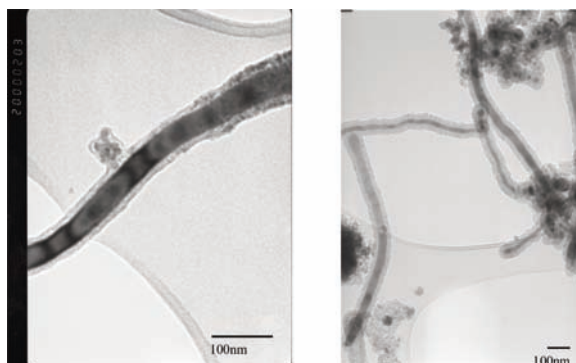
#### 4. Role of lithium batteries in electric vehicles

It has been estimated that in order to advance from gasoline powered vehicles, it is necessary to develop better batteries. An examination of the earth's resources shows that, out of all the known batteries, only lithium based batteries have sufficient resources to meet the demand to power billions of vehicles (Table 1) [11]. However, existing batteries need to be considerably improved to compete with the internal combustion engine. One possible area of improvement is the anode where the capacity is restricted by the solubility of lithium in graphite which gives the maximum capacity of the anode as 372mAh/g. Tin, silicon, aluminium and other metals can form intermetallic compounds of the type  $\text{Li}_4\text{M}$  with capacities up to 2000mAh/g. However, the insertion and de-insertion of lithium into the metals causes very large volume changes which causes the material to decrepitate into smaller and smaller particles which lose electrical contact [12].

**Table 1.** Number of vehicles that can be powered by the world resources of Pb, Ni, rare earth elements, Li and Cd.

Pb Acid	2.2 billion vehicles
NiMH	1.8 billion vehicles
Lithium-ion	12 billion vehicles
NiCd	0.049 billion vehicles

Furthermore, these compounds, when fully charged with lithium, can react with the electrolyte. One way of overcoming the disintegration of the intermetallic compounds and, at the same time, avoiding direct contact of the intermetallic with the electrolyte is to encase the compounds inside carbon nanotubes which are extremely strong and may contain the large volume changes and still retain



**Figure 3.** Tin filled carbon nanotubes and nanoparticles formed from graphite by electrolysis in LiCl [15]

electrical connectivity. This filling can be achieved by making graphite the cathode in a bath of lithium and tin chlorides as was discovered by Hsu who produced metal filled carbon nanotubes and nanoparticles [13]. This approach has been recently improved and is now being scaled up to produce commercial quantities of these materials by having two electrodes which were alternatively the anode and cathode [14]. The assumed mechanism for the formation of nanotubes and nanoparticles was that at the cathode, lithium intercalates into the structure forcing out sheets of graphite which roll up to form nanotubes or scrolls. Eventually, the surface of the cathode would become saturated with lithium and a lithium layer formed which prevented the intercalation of the lithium and the production of nanotubes ceased. When the electrodes were alternatively an anode and cathode this effect was prevented and nanotubes were continually produced (Fig. 3) [15]. Even with current reversal, the presence of tin chloride in the melt ensured the formation tin filled nanotubes. When anodes were made of these materials, it was found that the capacity was significantly improved, even after many charge-

discharge cycles (Fig. 4) [15]. The capacity of a graphite anode is around 350 mAh/g. Post mortem examination of the anode, after use, showed that the lithium must have diffused, via the walls, into the interior of the nanotube, reacted with the tin, causing it to expand which, in turn, caused the diameter of the nanotube to expand. On discharge, the lithium tin particles contracted but still remained in contact with electronically conducting nanotube. Furthermore, the nanotube prevented direct contact between the intermetallic and the electrolyte and prevented reaction between the lithium intermetallic compound and the electrolyte when the battery was fully charged.

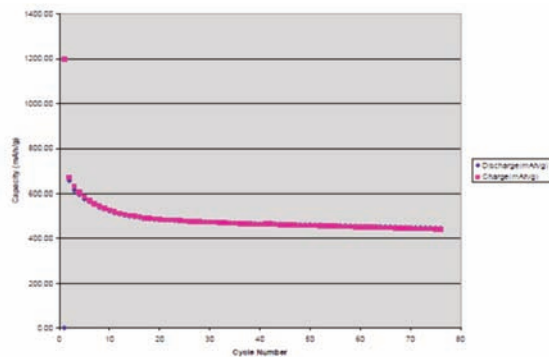


Figure 4. Performance of lithium tin anode [15] battery

The present demand for lithium is around 30,000 tonnes/year but if the number of vehicles powered by lithium ion batteries expands to billions, the amount of lithium metal produced must expand in tandem. The world's largest resource of lithium resides in South America in dehydrated lakes. At present, the lithium is precipitated from the brines as lithium carbonate which is then chlorinated to lithium chloride [16]. This is then electrolysed in a two electrode cell to produce lithium metal and chlorine. As both lithium and chlorine are less dense than the electrolyte, the anode and cathode distance is relatively large increasing the energy consumption and any increase in demand must increase interest in cheaper and more energy efficient methods of extracting lithium. It is difficult to separate the chlorine from the lithium as both rise up through the electrolyte. One possible way of doing this is to spin the carbon anode and stainless steel cathode which is wetted by molten lithium [17]. Under the imposed centrifugal field, the chlorine gas is encouraged to the centre of the reactor where it escapes, whereas the lithium is restrained by surface properties to the stainless steel until the force created by the spinning electrode and the difference in densities overcomes the surface forces and the lithium is radially projected into the electrolyte and rises up in the melt at a

different position to that of the chlorine. A schematic of a cell with rotating electrodes is shown in Fig. 5 [17] and the behaviour of a less dense fluid on a rotating wetted plate, immersed in an aqueous electrolyte, is shown in Fig. 6 [18]. In this way, it is possible to greatly decrease the anode to cathode distance so that the resistance losses in the melt are substantially reduced. An alternative way is instead

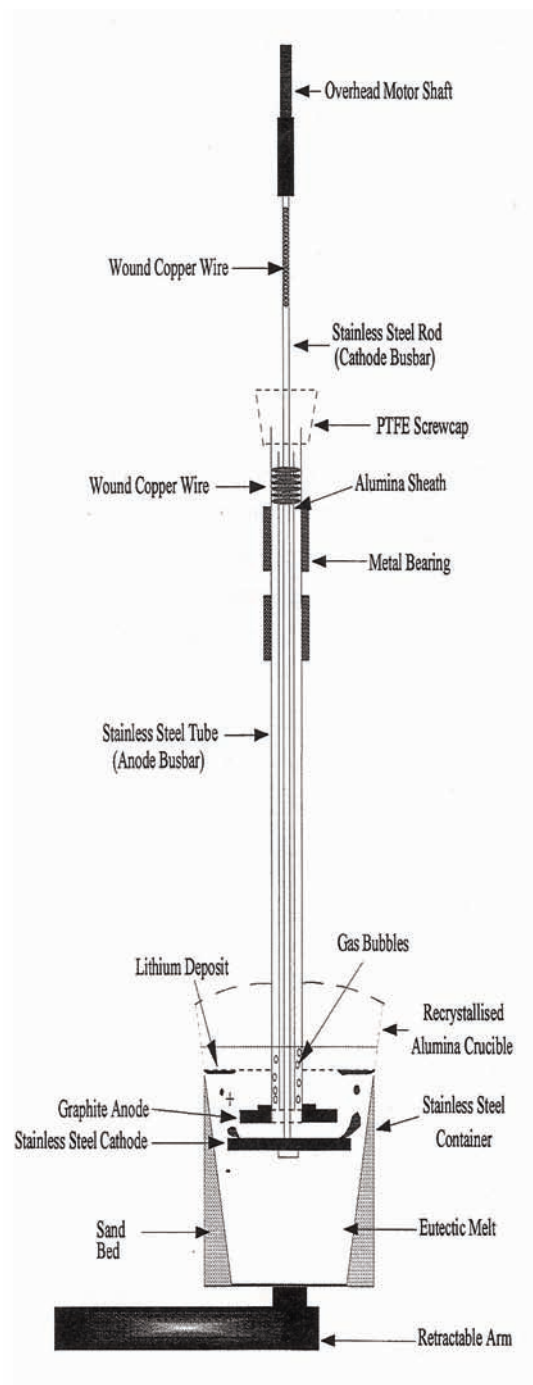
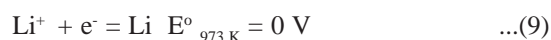


Figure 5. Schematic of centrifugal electrolysis



of changing the cell design is to change the electrolyte. The product of the purification process for lithium salts from brines is lithium carbonate which is subsequently chlorinated to the chloride. Lithium chloride is more expensive than lithium carbonate and it would be advantageous if this could be electrolysed to lithium but, unfortunately, the cathodic potential to decompose the carbonate ion is less cathodic than the potential to deposit lithium:



However, by arranging a porous diaphragm around the cathode, it was possible to ensure that there was minimal diffusion of the carbonate ion to the cathode and lithium could be electrowon at a current efficiency of 90% [19].

Obviously, if lithium ion batteries are used on a very large scale, it is important that the batteries are recycled at the end of their life. Up to now, the major emphasis on the recycling has focused on the recovery of highly valuable cobalt that is used for the cathode in the form of  $\text{LiCoO}_2$ . However, with the change to the much cheaper  $\text{LiFePO}_4$  as the cathode, the emphasis is likely to change to recycling the lithium. Some papers already describe methods for the capturing of lithium from used lithium ion batteries [20,21].

## 5. General Discussion and Conclusions

This paper has shown that molten salts, especially lithium based salts may, in conjunction with carbon, play a major part in the use of intermittent renewable energy. Carbonate fuel cells for converting the energy from hydrogen and hydrocarbons to electrical energy have been investigated for decades and although some problems still exist, these fuel cells have established themselves as probably the most successful as far as power output is concerned. This design of fuel cell, with minor modification, may also offer the ability to convert carbon dioxide, either from a power station but also from the ambient air, to carbon monoxide which can stored and either used for energy generation or the production of valuable chemicals.

High temperature batteries have been proposed before but the low voltages that are generated coupled with a high rate of self discharge have prevented their use. Molten salt cells based upon alkali or alkaline earth metals and air may make their adoption more feasible.

Finally, the combination of graphite and lithium allows the production of metal filled carbon nanotubes which can increase the capacity of lithium ion batteries and with increased use, the need for better recycling techniques.

Finally, in the future, the use of lithium is likely to be a major method for storing energy and this is likely

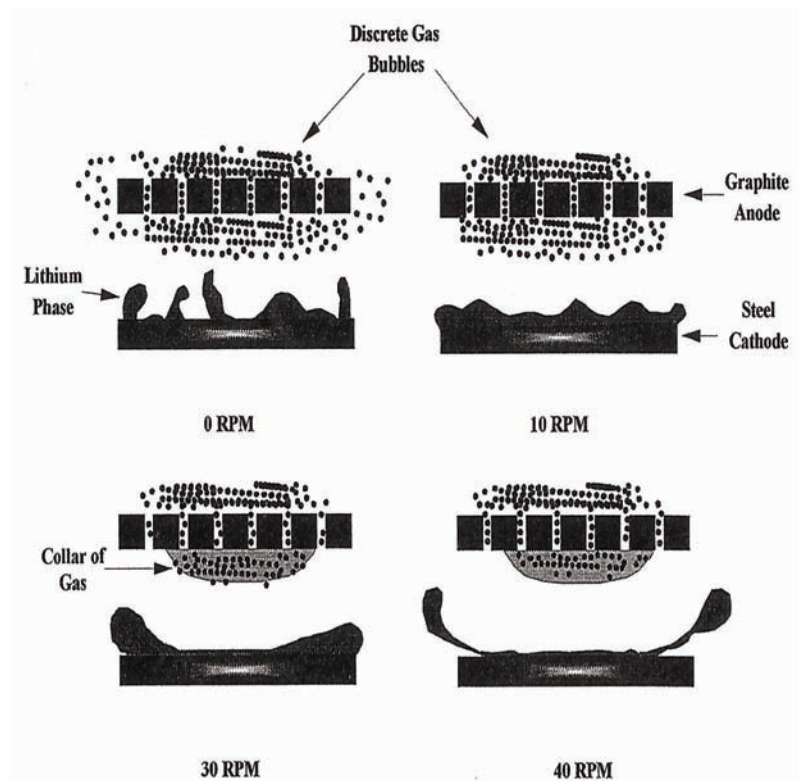


Figure 6. Schematic of distribution of phases as a function of rotation speed [17].

to lead to a need for improved more energy efficient methods for its extraction from molten salt electrolytes.

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