

The development of a carbon–air semi fuel cell

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Abstract

The increasingly demanding requirements of a number of military applications mean that there is a need for more energy dense power sources that is unlikely to be satisfied with conventional battery chemistries. A high temperature electrochemical power source employing carbon as a fuel has been identified as a technology offering a step change in available energy density.

Direct carbon conversion is an approach being pursued by several groups in the US. This paper discusses the state-of-the-art in this technology, and describes work carried out at Dstl and St. Andrews University to establish a new carbon–air semi fuel cell concept. This forms part of a four-year programme to develop a 50 W, 500 Wh demonstration unit.

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1. Introduction

High energy density power sources are required by a number of branches of the UK armed forces, including special forces in remote theatres of operations and future infantry soldiers (to power electric and electronic war-fighting aids and unmanned micro-air vehicles). There is a demand for both small, man-portable devices as well as larger battery chargers, e.g. for forward support of batteries for the BOWMAN radio system. In addition, new low cost, high performance, thermal reserve batteries are also required for shells, missiles, ejector seats and emergency power. In all of these applications, increasing the energy density of the power source will extend mission duration and enhance operational effectiveness.

Dstl has identified a high temperature electrochemical power source, operating on carbon as a fuel, which is capable of meeting the requirements of these demanding applications. It is applicable in two modes of operation: as a fuel cell, in which carbon is continuously supplied, or as a semi fuel cell,

operating on a limited amount of resident carbon. Following a feasibility study at St. Andrews University, a 4-year programme of work between St. Andrews and Dstl to develop a 50 W, 500 Wh carbon–air semi fuel cell (CAFC) is underway. A semi fuel cell forms the initial focus of this programme because the technical hurdles required to achieve short-term operation are less.

The research so far has been targeted at determining the promise of a new concept and establishing the best electrolyte choice for the 50 W unit. There are no weight targets for the first demonstrator, but the theoretical specific energy of the fuel, based on the free energy of carbon oxidation, is 9100 Wh kg⁻¹. For reasons that have been well documented [1], the efficiency of the cells and utilisation of the carbon, can be very high in direct carbon–air technology. This leads to the conclusion that a stack can be built, which can achieve a maximum fuel only specific energy of 7200 Wh kg⁻¹. The ultimate challenge will be to engineer a system containing 30–40% of stored fuel for a device specific energy of around 2000–3000 Wh kg⁻¹, a factor of 6–8 better than the best in-service primary batteries, and 20–30 times higher than the BOWMAN lithium-ion rechargeable.

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Table 1
CAFC electrode reactions

Electrolyte	Cathode reaction	Anode reaction	Overall reaction
Molten carbonate	$O_2 + 2CO_2 + 4e^- \rightarrow 2CO_3^{2-}$	$C + 2CO_3^{2-} \rightarrow 3CO_2 + 4e^-$	$O_2 + 2(CO_2)_{cath} + C \rightarrow 3(CO_2)_{an}$
Molten hydroxide	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	$C + 4OH^- \rightarrow 3CO_2 + 4e^-$	$O_2 + 2(H_2O)_{cath} + C \rightarrow CO_2 + 2(H_2O)_{an}$
Solid oxide	$O_2 + 4e^- \rightarrow 2O^{2-}$	$Sn + 2O^{2-} \rightarrow SnO_2 + 4e^-$ $SnO_2 + C \rightarrow Sn + CO_2$	$O_2 + C \rightarrow CO_2$

2. Existing carbon–air technology

Efforts to develop an electrochemical power source that can accept carbon directly as a fuel date back more than 100 years, the electrochemical oxidation of carbon having been studied and patented by Edison in 1891 [2] and Jacques in 1896 [3]. Early attempts failed to produce a practical device owing to the poor power densities obtained and the fact that non-volatile impurities in the carbon built up in the electrolyte and poisoned the cell. Today the technology is generally being pursued as a fuel cell for stationary power generation, with the intention of fuelling the cells with pure carbon obtained from the decomposition of hydrocarbons.

CAFCs employing three distinct electrolyte types have been described in the literature. The electrolytes, together with the ideal electrode reactions employed are listed in Table 1.

A carbonate-based CAFC was described by Cooper et al. [4]. It uses a molten alkali metal carbonate eutectic mixture as electrolyte and therefore operates at around 700 °C. A second CAFC variant, utilising a molten hydroxide electrolyte, was described in a patent by Pesavento [5]. The lower melting temperature of this electrolyte, together with good ionic conductivity, results in a CAFC operating at only 450 °C. The third electrolyte type is a solid oxide electrolyte, such as that described in a patent by Tao [6], and requires temperatures around 700 °C or more. A tin intermediate is known to be feature of this technology. Regardless of the electrolyte type, the overall cell reaction is oxidation of carbon to give carbon dioxide, a four-electron transfer.

The most important problems with both the hydroxide- and carbonate-based cells are corrosion of materials and degradation of the electrolyte. However, these should not be such a problem if the device is run as a one-shot battery, where the operational lifetime is short, hours rather than months, but requires specialist materials for longer term usage.

The carbonate electrolyte has the advantage that issues of electrolyte stability and compatibility with materials have already been solved, or partly solved, in molten carbonate fuel cell (MCFC) systems, minimising the number of technical hurdles required to develop a practical CAFC. Standard MCFC materials, such as lithium aluminate electrolyte matrices and lithiated nickel oxide cathode can be used. Lawrence Livermore National Laboratory (LLNL) is developing this concept, having reported cell performances close to 100 mW cm⁻² at 0.8 V [7] when operating on carbon black fuels. Problems associated with the distribution of electrolyte have been solved in operating 60 cm² cells with a

tilted geometry. Furthermore, LLNL has made the useful step of incorporating reactive carbons into a rigid block anode, whilst maintaining good electrochemical properties.

The hydroxide electrolyte can be chosen from a range of alkali metal and alkaline earth metal hydroxides. It is known to be intrinsically unstable towards carbonate formation in the presence of carbon dioxide reaction product, but reportedly can be stabilised for thousands of hours by humidification and addition of acidic oxides [8]. The lower temperature of operation of this electrolyte means that the range of materials applicable for the rest of the cell is widened. Scientific Applications and Research Associates has developed cells based on this electrolyte through several prototype iterations, obtaining a maximum of around 25 mW cm⁻² at 0.5 V [8].

The oxide electrolyte has the advantage that it is a solid, and therefore easier to handle than the liquid electrolyte systems. The liquid carbonate and hydroxide electrolytes require special measures to immobilise and manage them. The optimum distribution of electrolyte is assured if it is solid and the electrolyte can form a structural component of the cell. The oxide system is being developed by CellTech Power, a two cell tubular cell stack having been demonstrated [9].

3. System considerations

The CAFC is a high temperature device, in order to facilitate sufficient reactivity from the carbon and ionic conductivity from the electrolyte. The device must therefore carry a pyrotechnic compound that can be used to heat it up when first activated. Minimising the weight demands that only enough pyrotechnic be carried to achieve one heating cycle, i.e. the CAFC will be a one shot device with no thermal cycling allowed, the temperature to be maintained for the operating duration.

Because the CAFC is a high temperature device, heat loss is an issue. The desire to keep the device small means that the amount of heat insulation will be limited. It is likely therefore that a device as small as 50 W will not be thermally self-sustaining. However, the initial ambition is only to maintain the temperature sufficiently high for up to ten hours of operation. Nevertheless, it will be important to recuperate waste heat from the exhaust and pre-heat incoming air.

The main components of a carbonate-based system are shown in Fig. 1. This consists of the stack, a heat exchanger and an air blower. The relative number of molecules of gases in the process streams, per atom of carbon oxidised are also shown in Fig. 1 and assume an air excess of two. Table 1

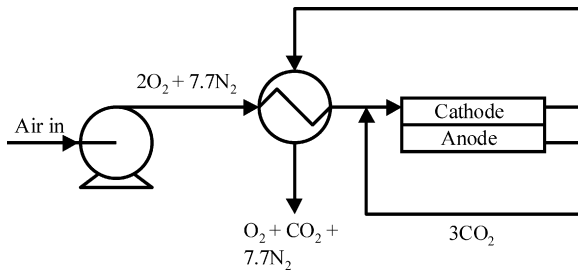


Fig. 1. Carbonate based CAFC system.

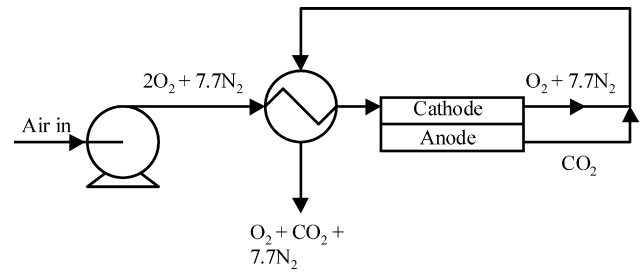


Fig. 3. Oxide-based CAFC system.

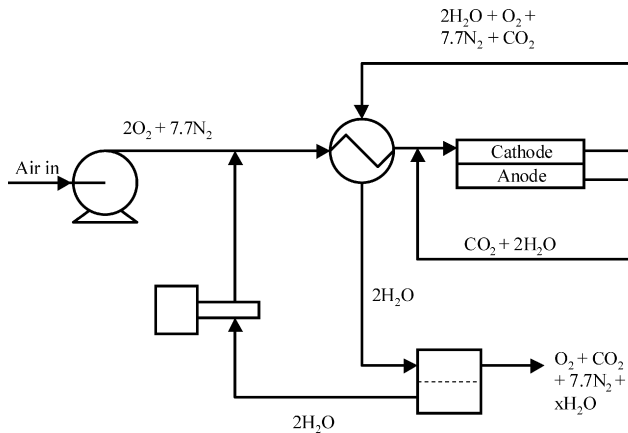


Fig. 2. Hydroxide based CAFC system.

indicates that for each atom of carbon oxidised at the anode, two molecules of carbon dioxide are required at the cathode and three molecules of carbon dioxide are discharged at the anode. The anode exhaust must therefore be routed to the cathode to avoid carrying carbon dioxide as a cathode reactant.

Similarly, the hydroxide system also requires a reactant other than oxygen at the cathode, namely steam. This is regenerated in full at the anode, so that provided the cathode is tolerant of carbon dioxide, routing the anode exhaust to the cathode will provide steam in the stoichiometric amount. However, some water would need to be carried to provide steam in excess, which would be necessary to avoid Nernst effects. Minimising the amount of extra water carried will necessitate the recycling of water condensed from the cathode exhaust. Therefore, a water pump and separator are additional items required in this system. It can be seen that this is now a significantly more complex system (see Fig. 2).

The oxide system is potentially the simplest of all. The electrochemistry is such that only oxygen is required at the cathode and carbon at the anode so that no recycle loops are required. Instead, the cathode and anode exhausts can be commoned for the purposes of heat exchange, and the system shown in Fig. 3 obtained.

Table 2 contains the results of modelling the systems in Figs. 1–3. The intention of this modelling was to ascertain the relative merits of the electrolyte choice from the point of view of heat loss in the exhaust and the requirement to carry additional reactants. Gross simplifications that were made concerning other aspects of the systems included an isothermal stack, no heat losses elsewhere in the system, an 80% stack voltage efficiency, and 15 W parasitic power in air blower, sensors and controls. It was further assumed that the systems are supplied with dry air at 20 °C. The performance of the heat exchanger was assumed to be that recently published for a unit at this scale [10].

It can be seen from Table 2 that the carbonate and oxide systems present similar thermal management problems, a consequence of the similar exhaust composition. The hydroxide system produces a relatively cool exhaust, because waste heat is locked up in the enthalpy of vapourisation of steam, owing to the fact that not all of the steam can be condensed from the stack outlet. However, this steam loss necessitates a reservoir of 103.4 g of water (c.f. the carbon requirement of 89.3 g). The effective theoretical specific energy of the reactants is then only 4200 Wh kg⁻¹. This would likely result in a system well below the target specific energy. Whilst additional heat exchange arrangements could be put in place to condense additional steam, this would make a complicated system even more complex. On this basis, the hydroxide system is not favoured for portable applications.

Table 2
Modelling of 50 W, 500 Wh CAFC systems

System	Cathode excess	Water required (g)	Exhaust temp (°C)	Rate of exhaust heat loss (W)
Carbonate at 700 °C	2:1 (O ₂) 1.5:1 (CO ₂)	0	184.7	10.1
Hydroxide at 450 °C	2:1 (O ₂) 1.5:1 (H ₂ O)	103.4	39.8	8.4
Oxide at 750 °C	2:1 (O ₂)	0	198	10.9

4. St. Andrews/Dstl solid oxide CAFC concept

In order to gain experimental experience that will enable an informed choice between the electrolyte systems, St. Andrews University have operated cells of each type. On the basis of this experience a cell concept has been proposed in order to overcome the principal difficulties encountered. This is effectively a combination of oxide and carbonate cells, comprising a solid oxide electrolyte, and a liquid anode consisting of carbon particles dispersed in a secondary electrolyte of molten carbonate. This system has the following advantages:

1. The oxidant gas stream remains undiluted since the cathode reaction only involves oxygen, increasing the available cell potential. For example, the cell would theoretically develop 36 mV higher open circuit potential than the system depicted in Fig. 1, assuming ambient pressure air feed. A slightly more compact design would be possible by removal of the recycle loop necessary with the carbonate system.
2. The less complicated cathode reaction does not require multiple species to come together for reaction at the three-phase boundary. Therefore, there should be more scope for rapid reaction kinetics than with hydroxide or standard carbonate systems.
3. A wider selection of materials is available. For example, the cathode does not need to be resistant to corrosion by the carbonate melt, as it is never exposed to that environment. Furthermore, other carbonate mixtures, which would be excluded from the standard MCFC cell, owing to their severe dissolution of the cathode, are applicable in the CAFC.
4. Electrolyte management is made much easier. There is no need to meticulously maintain electrolyte levels as

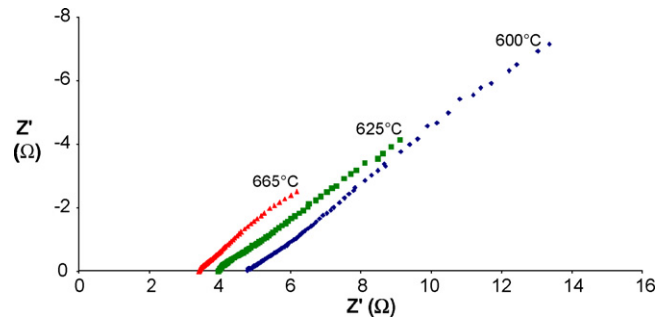


Fig. 5. Impedance data from the oxide system.

the cathode can never be swamped by, or starved of, carbonate.

5. Cell testing

The concept described above was evaluated in several cell configurations. An early set-up is shown in Fig. 4. This cell utilised a platinum paste cathode applied to the inside surface of an yttria-stabilised zirconia (YSZ) tube, although any suitable solid oxide electrolyte can serve, including lanthanum–strontium, gallium–magnesium oxide or, ceria–gadolinia. The cathode was 35 cm² in area. The tube was immersed in the molten carbonate, contained in a nickel body, and in which super S carbon black was dispersed in an 8:1 molar ratio. The anode consisted of a nominally 1 cm² mesh of nickel, the standard anode material for MCFCs, with a gold current collecting wire. This arrangement was chosen as the mesh allows free circulation of the carbonate.

Fig. 5 gives impedance spectra obtained with this cell as it was heated to 665 °C. The spectra are clearly diffusion domi-

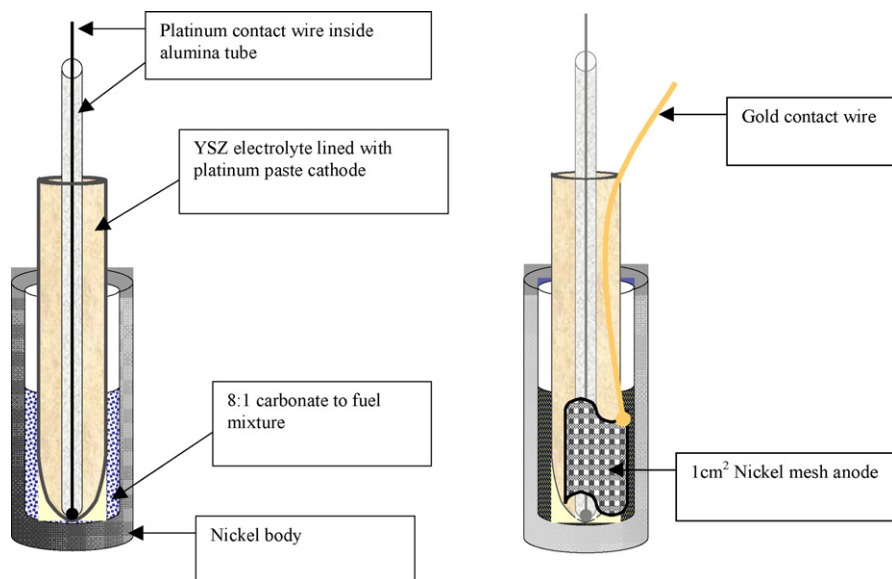


Fig. 4. Experimental cell set-up.

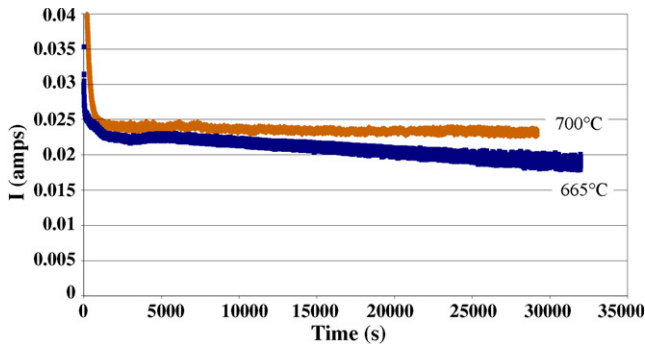


Fig. 6. Potentiostatic polarisation of a solid oxide cell at 0.5 V.

nated, as would be expected with the anode slightly displaced from the solid electrolyte. The spectra show the expected decreasing cell resistance as the temperature increased.

Fig. 6 gives the results of potentiostatic tests at 500 mV, obtained at 665 and 700 °C. It can be seen that the current decayed slightly with time at 665 °C. This is probably due to the build up of carbon dioxide bubbles, since the original performance could be restored with a little agitation. The unstable current could also be a consequence of the disturbance caused by carbon dioxide bubbles being discharged from the anode. The current was more constant at 700 °C and the instability less. This may be a result of the bubble disturbance being less because of the lower carbonate viscosity at this temperature.

The current obtained was relatively modest, around 22 mA at 0.5 V, equating to around 10 mW, and an area specific resistance of around $17 \Omega \text{ cm}^2$. About $4 \Omega \text{ cm}^2$ can be ascribed to the electrolyte, with the remainder due to electrode performance. The zirconia electrolyte is resistive because a relatively thick electrolyte layer was used. Thinner electrolytes would reduce this resistance. Furthermore, there is clear scope for optimisation of the other cell components, e.g. employment of standard solid oxide cathodes and development of the anode electrochemistry. But overall the concept looks promising and the main technical hurdle of showing a viable solid electrolyte/liquid electrode concept has been overcome.

6. Materials stability

Molten alkali metal carbonates are very corrosive. Degradation of cell performance as a result of unwanted corrosion reactions is therefore an issue, even for the relatively short duration of operation envisaged in the target applications. For example, nickel is known to display some solubility in these systems [11] and this limits the life time of the cell. It is therefore desirable to find other compatible materials.

It has been reported that, under reducing conditions, silver shows no significant solubility in molten carbonate systems. Under aerobic conditions and with no reducing species present, we found that silver was slightly soluble (to ppm

level) in the lithium potassium carbonate eutectic mixture. This was determined by extracting small samples from the carbonate, which had a silver wire immersed in it, dissolving the sample in 10 wt% HCl, and determining the silver concentration by atomic absorption spectroscopy (AAS). However, on final weighing of the wire, the mass of the silver used was essentially unchanged. This was due to the formation of a surface layer of oxide.

A similar procedure was used to establish the solubility of a steel tube. Visibly, however, it is apparent that the material dissolved considerably in a very short space of time (with a concomitant browning of the carbonate mix). It is reported that under reducing conditions the following stainless steels are unaffected in the lithium/potassium carbonate mixture: 347, 310, 316, 321 and 304 [12]. Steels may therefore be more suitable on the anode side.

It was found that the standard YSZ electrolyte was not stable in molten carbonate. Small sections cut from a YSZ tube and immersed in Li/K carbonate eutectic mixture at 700 °C, progressively absorbed lithium over a 10-day period, according to analysis using an inductively coupled plasma mass spectrometer (see Fig. 7). X-ray diffraction analysis indicated conversion of the YSZ to lithium zirconate.

One obvious answer to the above problem is to switch to an alternative solid oxide electrolyte. Many such materials have been reported in the literature, often motivated by the desire to reduce the operating temperature of solid oxide fuel cells. Fig. 8 shows the conductivity of a number of these, and it can be seen that some exhibit better ionic conductivity than YSZ, and these are potential electrolytes for the CAFC.

A test programme is underway to ascertain suitable materials combinations. Test mixtures were heated to high temperature for 24 h and the structural changes determined by XRD. The initial results are shown in Table 3.

Table 3 indicates that YSZ is stable in the alternative sodium/potassium carbonate eutectic. This can be considered as the secondary electrolyte at the expense of slightly less favourable electrochemical properties. Ceria appeared to be stable in both of the eutectics. However, although no obvious structural change was observed from the XRD results,

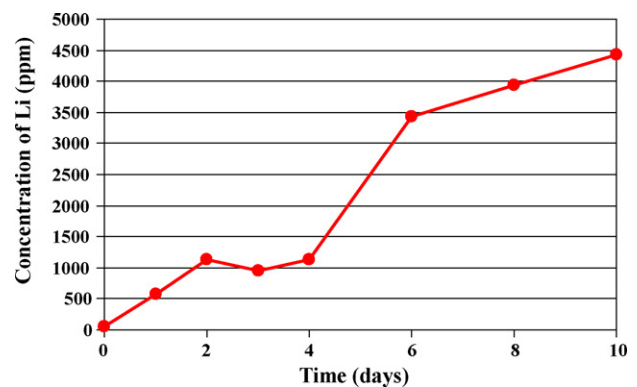


Fig. 7. Concentration of Li ions absorbed by YSZ samples immersed in carbonate at 700 °C.

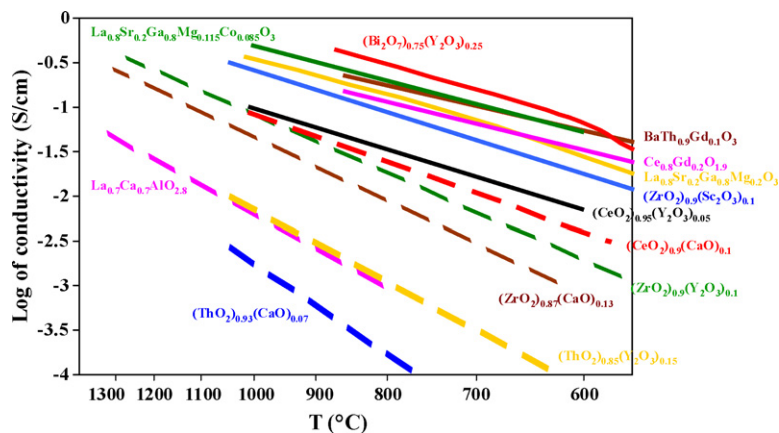


Fig. 8. Oxygen ion conductivity of YSZ and alternative electrolytes under air [13–15].

Table 3
Results of heating various mixtures for 24 h

Mixture	Temperature	Change
CeO ₂ + Li ₂ CO ₃ /K ₂ CO ₃	700	No change
CeO ₂ + Na ₂ CO ₃ /K ₂ CO ₃	750	No change
YSZ + Li ₂ CO ₃ /K ₂ CO ₃	700	Lithium zirconate
YSZ + Na ₂ CO ₃ /K ₂ CO ₃	750	No change
NiO + CeO ₂	800 (Oxidising conditions)	No change
NiO + CeO ₂	800 (Reducing conditions)	Ni + CeO ₂

it is reported that the exposure of ceria to molten carbonate causes species, such as Ce₁₁O₂₀ and Ce₆O₁₁ to be formed [11].

7. Summary and future work

The combined oxide/carbonate carbon–air concept has been shown to hold promise, having achieved 10 mW cm⁻² from unoptimised cells, and stable operation over the ten hours required. It is planned to develop this concept further by:

- Examining alternative solid oxide electrolytes that may offer better ionic conductivity and compatibility with lithium-containing molten carbonates.
- Developing the anode further by employing alternative carbonate or molten oxide formulations that may offer improved electrochemical properties and/or better wetting behaviour with the carbon.
- Optimising the cell to obtain the maximum in power density.

The cells will then be assembled into stacks and tested for performance and durability, normally and in the presence of battlefield contaminants in the air stream. The fuse

and pyrotechnic will then be specified along with the insulation and heat exchanger needed to ensure close thermal management. A 50 W system will then be assembled and tested.

Acknowledgement

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