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Batteries for Venus Surface Operation

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The surface of Venus is one of the most challenging environments for the operation of spacecraft. With a surface temperature of around 460°C and a surface atmospheric pressure of 92 bar of carbon dioxide, conventional power technologies are not usable. A number of battery technologies can be adapted to the high-temperature environment. A new primary-battery technology for Venus surface operation is proposed, which uses the in situ carbon dioxide atmosphere as a reactant. This technology would allow high-specific-energy density and, thus, extend the operating time of a battery-powered Venus surface mission.

I. Introduction

THE planet Venus is an interesting target for scientific exploration; it is both similar to Earth in terms of composition, size, and location in the solar system, and very different from Earth in its atmosphere and climate. There are many unexplained scientific questions about Venus that could benefit from further exploration, including missions to the surface. With an average surface pressure of 92 bar and an ambient temperature of between 390 and 485°C [1], the surface of Venus is a difficult environment for the operation of a probe. Long-duration missions to the surface of Venus present a significant challenge to the power system.

Previous missions to Venus have survived on the surface for only a limited duration [2]. Russian missions, including probes in both the Venera and Vega series of spacecraft, have successfully landed on the surface of Venus, but the longest-lived of these Venus missions, Venera 13 (1978), transmitted from the surface for only 127 min. Although the loss of transmission came because the radio-relay spacecraft moved out of range, the Venera spacecraft were not designed to operate for significantly longer periods of time, because the electronics, power system, and radio were not capable of operating after the spacecraft reached temperatures above the nominal operating temperatures. The pressure vessel containing the electronics and battery incorporated thermal insulation and phase-change material to increase the thermal mass, and the electronics and battery were destroyed as the cumulative heat leaked into the spacecraft brought the interior temperature toward ambient. Likewise, although one of the U.S. Pioneer Venus mission small probes operated on the surface Venus for 67 min, this probe was also not designed to operate after the interior reached high temperatures [3].

A number of future missions have been proposed to explore the surface of Venus, ranging from drop probes and stationary landers [4], to rover missions [5], to missions designed to return a sample from the Venus surface to Earth [6]. The Space Studies Board "Decadal Study" ranked a Venus Surface In Situ Explorer as one of the five highest priorities for medium-class future missions [7].

If such a mission is to operate for significantly longer than the 1–2 h surface survival of previous missions, it will be necessary for the mission develop new approaches to withstand the high-temperature environment. Although one approach to long-duration missions to the surface of Venus is to design a mission that uses a radioisotope power source to power a refrigerator or cooler to reduce the temperature of the electronics and power system to an environment at which conventional electronics operate [8–10], another approach would be to develop systems that can operate in the high-temperature environment. Electronics that can operate in the Venus environment are being developed and include high-temperature SiC transistors, which have now been tested for operation at 500°C with test durations exceeding 2000 h [11].

It would be desirable to develop power systems that can be used on the Venus surface for long durations. A significant component of any such power system would be chemical energy storage, or batteries, which can operate on Venus. Battery storage systems are required for many applications. For mission durations of a few weeks to possibly as long as a year (for very low-power systems), batteries could serve as the primary power system for the mission. For longer missions that may use other prime power sources (e.g., radioisotope power sources), batteries may still be needed for high-power deployments, for example, for actuation of mechanical parts after landing on the surface. These applications can be achieved with primary batteries.

Secondary batteries may also be useful on Venus missions. Secondary batteries can be used to buffer power, so that a primary power source that provides low but constant power can store energy for transient high-power events. Such events will include motor startup transients, deployments, short-duration operation of high-power instruments such as lasers, and high-power operation of radio transmitters.

The environmental conditions on Venus depend somewhat on the area chosen for the landing. Although the average temperature is 462°C at a pressure of 95.6 bar, the temperature reduces to as low as 390°C at a pressure of 48 bar at the highest altitude on Venus, which is Maxwell Montes, 10.4 km above the average altitude [1]. Likewise, the temperature and pressure increase if a landing at the lowest point of Venus is chosen (i.e., about 485°C at the bottom of Diana Chasma, 2.9 km below the mean level). There is little diurnal variation in temperature, and the temperature and pressure are only weakly dependent on latitude.

The criteria for the evaluation of Venus battery technologies are as follows:

1) It must operate at Venus temperature. For the average surface temperature of Venus, this requires operation at roughly 460°C (slightly lower if the battery is to operate only at the highest-altitude locations).

2) It must operate at Venus atmospheric pressure, approximately 92 bar of carbon dioxide.

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3) Exterior casing of the battery must withstand chemical corrosion of an atmosphere of high-pressure carbon dioxide at 460°C, with likely trace components of sulfur oxides and hydrogen sulfide. (Although the Venus clouds contain concentrated sulfuric acid droplets, sulfuric acid is not likely to be found in the surface environment because it decomposes into sulfur trioxide at 340°C.)

4) It must have a high specific energy, expressed in watt-hour per kilogram (where $1\ \mathrm{W \cdot h/kg}$ equals $3.6\ \mathrm{kJ/kg}$).

5) It must have robust technology; the battery will need to withstand the launch, entry, and landing environment, including vibration, shock, and acceleration loading.

6) It must have high technology readiness; it is desirable that the state of development of the battery be at or near production readiness, with little or no additional research needed to reach flight-ready technology.

7) It must be capable of meeting flight-qualification requirements for space.

In this paper, we will review possible technologies for the use of batteries on the surface of Venus and propose a possible new battery chemistry that will use the environment of Venus as a reactant to achieve high specific energy.

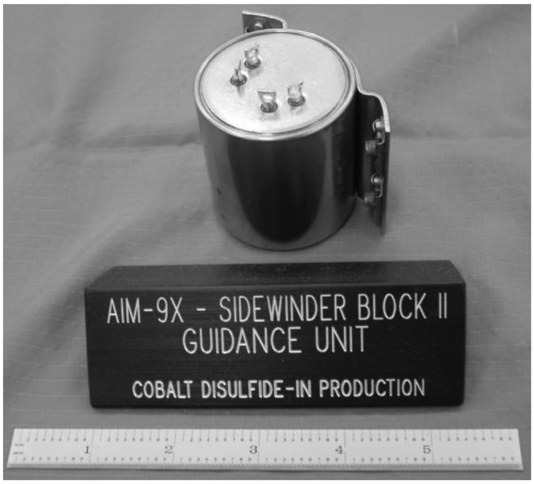

Fig. 1 Production unit of a small thermal battery using cobalt-disulfide chemistry (Image courtesy ENSER Corporation, Cinnaminson, NJ).

II. Primary Batteries for Venus

At Venus temperature, the aqueous-electrolyte chemistry of the batteries used in all existing satellite and space applications is not usable. At these temperatures, however, molten-salt electrolytes are a feasible chemistry. Molten-salt electrolytes are typically based on either halide (usually chloride) salts or sometimes on carbonates. The melting temperature of the electrolyte salt is adjusted by the use of mixed component salts, often in a eutectic mixture.

A number of molten-salt electrolyte batteries have been developed for use in terrestrial applications. In particular, the technology of "thermal batteries" is well developed.

An alternative to the molten-salt electrolyte technology is the use of a solid oxide electrolyte, typically an alumina-based material in which alkali ions and oxygen ions are mobile.

A. Thermal Batteries

Thermal batteries are a technology that has been extensively developed for Earth [12]. Because the battery technology uses a molten electrolyte at an operating temperature considerably higher than Earth ambient, the battery must be heated before use. This may be done by a pyrotechnic charge that produces an exothermic reaction, for example, an iron/potassium permanganate mixture set off before use. Because the energy-producing reaction cannot occur until the electrolyte is melted, the battery is not subject to self-discharge until it is brought to operating temperature by firing the pyrotechnic. Thus, these batteries have long storage life at ambient (Earth) temperature. These are used in applications for high-power, short-duration missions that may require long storage time before use. Typical applications are to weapons or one-time-use aerospace systems. Thermal batteries have been qualified and used on space missions, typically for high-current, low-duration applications; for example, the Mars Exploration Rover mission used $\mathrm{Li{-}FeS_2}$ thermal batteries for the pyrotechnic initiations on the descent.

For the Venus application, the initial exothermic pyrotechnic reaction to melt the salt electrolyte would not be needed. This would reduce the battery mass.

The electrolyte salts typically melt at temperatures between 319 and 436°C. A number of molten-salt electrolytes are used, with a LiCl–KCl eutectic that melts at 352°C being one very common electrolyte [12–14]. Another electrolyte system, a LiBr–KBr–LiF eutectic electrolyte, operates over a temperature range of 400 to 550°C [15].

Figure 1 shows an example of a thermal battery currently in production for weapons systems. Because these batteries are designed for weapons use, they are extremely rugged and far exceed spacecraft requirements for shock, vibration, and acceleration loads.

A typical chemistry for a thermal battery uses an alkali metal (typically Li) for the anode and a metal sulfide for the cathode. For example, the lithium–iron–sulfur batteries typically react in two stages [13], with a primary reaction of

$$2\mathrm{Li} + 2\mathrm{FeS} \rightarrow \mathrm{Li_2FeS_2} + \mathrm{Fe}(V^{\mathrm{o}} = 1.64\ \mathrm{V})$$

and a secondary reaction of

$$2\mathrm{Li} + \mathrm{Li_2FeS_2} \rightarrow 2\mathrm{Li_2S} + \mathrm{Fe}(V^{\mathrm{o}} = 1.62\ \mathrm{V})$$

for a net reaction of

$$2\mathrm{Li} + 2\mathrm{FeS} \rightarrow \mathrm{Li_2S} + \mathrm{Fe}$$

Another thermal battery chemistry, based on the sodium/metal chloride reaction, is discussed in Sec. III.B.

In general, the reactions used for thermal batteries are inherently reversible, and so in principle both primary and secondary cells could be made. Although the most common usages are single-shot use, and secondary thermal batteries are not in common production, U.S. Department of Energy and U.S. Air Force programs in the early 1980s that developed one of the technologies, $\mathrm{Li{-}Al/FeS_2}$, as a secondary battery that operated at 450°C [14,16].

Many of these batteries use lithium alloys for the anode, rather than elemental lithium [17]. Lithium aluminide or lithium silicides are commonly used.

A number of thermal battery chemistries suitable for Venus operation are available today. Some of these batteries are listed in Table 1. Except as noted, the specific-energy numbers listed are values achieved in existing batteries. Other chemistries, such as

Table 1 Thermal battery chemistries

Cathode	Anode	Electrolyte	Operating temperature	Specific energy, $\mathrm{W \cdot h/kg}$	Voltage, V	Reference
FeS	LiAl	LiCl–KCl	450°C	60–100	1.33	[17]
$\mathrm{FeS_2}$	$\mathrm{Li_4Si}$	LiCl–KCl	450°C	120–180	1.8/1.3	[17]
$\mathrm{FeS_2}$	$\mathrm{CaAl_{1.2}Si_{0.4}}$	$\mathrm{LiCl{-}NaCl{-}CaCl_2{-}BaCl_2}$	480°C	610 (theoretical)	2.0/1.2	[17]
$\mathrm{CoS_2}$	Li	LiBr–KBr–LiCl	450–480°C	70–120	1.97	[15–20]

calcium-metal sulfide [14], have been demonstrated at 450°C operation but not yet taken beyond the early developed stage.

B. Self-Discharge of Thermal Batteries

A significant problem with conventional thermal batteries may be self-discharge at operating temperature [21–24]. The typical mission for thermal batteries is for high-power, short-duration missions, and although the self-discharge rate during storage is extremely low, once the battery has been raised to operating temperature, self-discharge may be high. This could limit the mission lifetime and make conventional thermal batteries unsuitable for longer-duration missions. The self-discharge rate varies considerably depending on details of the battery construction; for example, Knödler [23] measured self-discharge rates of about 1% per day for fully charged engineering-scale LiAl/FeS cells at an operating temperature of 470°C, but noted that the rate goes down to about 0.5% per day when the battery is in a semicharged state and decreases with time when the battery is held at open-circuit conditions. Guidotti et al. [24], on the other hand, observed about a 25% loss of capacity for $LiSi/Fe_2S$ batteries held at open-circuit voltage for 1 h, although this rate was decreased considerably by the use of fused, lithiated catholytes, most particularly the LiCl/KCl electrolyte, for which the capacity loss decreased to about 2% over the 60 min test. Del Castillo, et al. [4] noted considerably higher self-discharge rates for the $Li\text{-alloy}/FeS_2$ cells they tested, with performance dropping within 40 min of operation.

A variant technology for a $Li\text{-alloy}/FeS_2$ thermal battery has been proposed [25], using a solid $(Li_3PO_4/LiSiO_4)$ electrolyte instead of the molten salt, and has been tested successfully at 460°C. The use of a solid electrolyte may be a means of reducing the self-discharge rate.

The self-discharge rate at operating temperature is an area that needs further study. Although not fully understood, self-discharge is apparently related to the dissociation of the FeS_2; a mechanism for self-discharge may be sulfur gas, sulfur ions (polysulfides), or sulfur-rich species leaving the cathode [22]. Self-discharge is also possibly related to a soluble iron specie dissolved in the electrolyte [22,24].

C. $LiCoS_2$ Thermal Batteries

A related chemistry, the $LiCoS_2$ thermal battery [15–20], has lower rates of self-discharge than FeS systems [12,21].

The $LiCoS_2$ thermal battery has now reached production readiness for commercial applications such as missiles. The battery uses a lithium alloy anode with a cobalt–disulfide cathode. The operating temperatures are from 400 to 550°C, most typically 450–480°. The primary discharge reaction produces Li_2S by reducing the oxidation state of the cobalt.

Specific energy as high as 120 $W \cdot h/kg$ is available in thermal batteries that are flight-qualified for a number of aerospace systems. As with other thermal battery types, for Venus application, the pyrotechnic reaction to melt the electrolyte would not be needed. This would increase the specific power.

D. Fluoride Chemistries

A new solid-electrolyte high-temperature battery chemistry [4,25] has been proposed based on a Ca anode and a NiF_2 cathode. This battery uses a solid electrolyte that is conductive to the fluoride ion, consisting of a solid solution of NaF-doped CaF_2 at an operating temperature of 450°C. Although prototype batteries have only been demonstrated in small-scale laboratory demonstrations, operation for six days of continuous discharge with little loss of voltage has been demonstrated. Theoretical open-circuit voltage for the anode/cathode combination is 2.93 V; the actual voltage measured was 2 V (under a load of 62.5 $\mu A/cm^2$) at the beginning of discharge, dropping to about 1.3 V at the end of the six-day discharge. The expected specific energy is predicted to be in the range of 280–400 $W \cdot h/kg$ [25].

Although not yet at a technology level ready for production, the chemistry may have an application in the future.

III. Secondary Batteries for Venus

A. Sodium–Sulfur Battery

An alternate high-temperature battery technology is the sodium–sulfur battery [17,26,27]. Sodium–sulfur batteries were initially developed as a high-specific-energy rechargeable battery system with a low self-discharge rate for electric vehicles. They are currently being demonstrated in electric utility applications [28] to serve as an energy storage system to store energy for use during peak demand periods. Such batteries have demonstrated hundreds of charge/discharge cycles with a low decrease in capacity.

The reaction sequence is a multistep reaction producing polysulfides. The initial reaction is [13]

$$2Na + 5S \rightarrow Na_2S_5 \qquad (V^o = 2.076)$$

Subsequent reactions produce a sodium-rich polysulfide, Na_2S_{5-x}, at a slightly lower voltage ($V^o = 1.78$ V) [10].

Current sodium–sulfur batteries use a beta-alumina solid oxide electrolyte. This electrolyte also serves as a separator between the liquid sodium anode and the liquid sulfur cathode. At operating temperatures above about 300°C, sodium ions are mobile in the solid-electrolyte material. Because of the relative impermeability of the solid electrolyte, the self-discharge rate of the NaS battery is extremely low. A schematic of the battery is shown in Fig. 2.

Because of the high specific energy, there has been some interest in the use of sodium sulfur batteries for space operation [29,30], despite the high temperatures. A potential difficulty of the NaS battery technology is the fragility of the beta-alumina electrolyte. A demonstration test of the sodium–sulfur battery in space was done on space shuttle flight STS-87 in November 1997. This is shown in Fig. 3. The experiment lasted 10 days and showed that the NaS battery could be successfully qualified for space operation and operate in space conditions.

Batteries for terrestrial application are available at a specific energy of 220 $W \cdot h/kg$, and a specific energy of over 300 $W \cdot h/kg$ is predicted for space batteries. The model tested on the shuttle had a typical specific energy of about 150 $W \cdot h/kg$ (see also [28]).

The typical operating temperature range for terrestrial applications is 290–390°C. The maximum temperature is set by the fact that both the reactants, sodium and sulfur, and the reaction product, sodium sulfide, need to remain liquid. The upper limit is set by the vapor pressure of sulfur, because the boiling point of sulfur at 1 bar is 444.6°C. Sulfur vapor pressure as a function of temperature is available in Chang and Jhon [31]. At Venus pressure of 92 bar, the boiling point of sulfur is about 988°C, and so the sulfur remains in liquid form at Venus surface temperature. The sodium vapor pressure at 450°C, 0.0019 bar, is well below the atmospheric pressure of Venus [32]. Finally, evaluation of the phase diagram of the NaS system shows that at 450°C all of the reaction products are in a liquid–liquid phase [26]. Thus, there should be no barrier to operation of a sodium–sulfur battery at Venus temperature and pressure, and in fact, operation of a sodium–sulfur battery at 460°C has been demonstrated at 92 bar pressure [33]. This will require that the sealed reactant reservoir of the battery be equilibrated to the Venus pressure.

The analogue chemistry using lithium also can be used, forming a lithium–sulfur battery [17]. This chemistry in principle has a high specific energy, but the technology is at a significantly lower level of development.

Thus, the sodium–sulfur battery, a high-energy-density battery that has a long history of development for applications on Earth and has been space qualified, is an excellent possibility for energy storage on Venus [5].

B. Sodium Metal Chloride Battery

Another high-energy secondary (rechargeable) battery technology currently being developed is the $Na/NiCl_2$ battery chemistry, using a $NaAlC_4$ molten-salt electrolyte [34,35]. This cell technology is under development for electric vehicle applications. Under the name "zero emission battery research activity" battery [34] (or ZEBRA

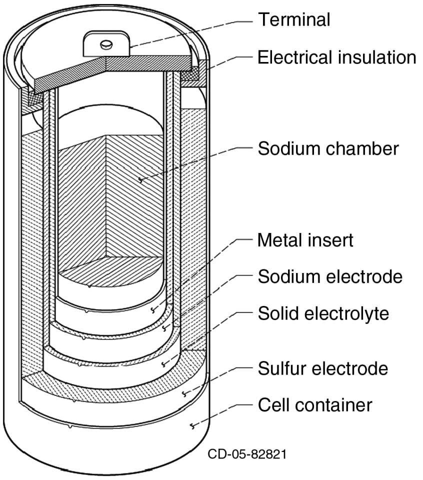

Fig. 2 Schematic cutaway diagram of a sodium–sulfur battery.

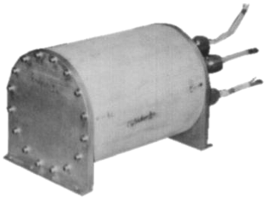

Fig. 3 Sodium–sulfur battery flown on a space shuttle test in 1997.

battery, as it is more commonly known), this battery is now being manufactured in prototype quantities. Like the NaS battery, the sodium metal chloride battery uses a beta-alumina solid electrolyte as a separator with sodium-ion conduction.

The sodium metal chloride batteries use a primary reaction of [13]

$$NiCl_2 + 2Na \rightarrow Ni + 2NaCl \qquad (V^o = 2.58\ V)$$

A similar reaction using $FeCl_2$ produces $V^o = 2.35$ V. Several other related chemistries have also been demonstrated.

Both the $Na/NiCl_2$ and $Na/FeCl_2$ chemistries have been demonstrated, although the $NiCl_2$ chemistry is preferred because of the wider temperature range of operation, 200–400°C [13]. The schematic of the $Na/NiCl_2$ battery is virtually identical to that of the NaS battery shown in Fig. 3, except that the Na anode is typically on the outside, whereas the $NiCl_2$ cathode is in the center. The cell voltage V^o is slightly higher than that of the NaS battery. Specific power has been demonstrated up to 143 $W \cdot h/kg$.

The technology development status of this battery for terrestrial applications is high, with an experience base of thousands of batteries built and many demonstration projects with over 15 years of experience. However, terrestrial batteries typically operate at the lower end of the temperature range, typically 270°C, although Pistoia [34] reported that 450°C operation of the $Na/NiCl_2$ battery is possible. Recent work by the U.S. Department of Energy [36] has tested single-cell $Na–FeCl_2$ batteries at temperatures of 500 and 600°C, with no failures after 7 h of operation at 500°C, and $Na–ZnCl_2$ for up to 50 h of operation at 425°C. However, comparatively little development effort has been done on the higher temperature range of operation, because high-temperature operation is not of interest for terrestrial applications.

IV. New Battery Technology

A. Lithium/Lithium Carbonate Battery

Considerably higher specific energy is possible by using a cell technology that uses ambient carbon dioxide as a reactant. By using materials available on Venus as one of the reactants in the battery, the material brought from Earth is effectively leveraged into a much higher amount of reactant available on Venus; hence, the effective specific energy can be significantly increased.

This mass leverage is most effective when the material brought from Earth is both a lightweight reactant and also is easily stored at Venus temperature and pressures. In terms of specific power, hydrogen is the lightest reactant that can be brought from Earth; however, hydrogen is not easily stored at Venus temperature. For this battery we consider the use of lithium, which is both the lightest of the alkali metals and also the one highest on the electrochemical series. Thus, oxidation of lithium is the alkali metal reaction with the highest inherent specific energy. Although other metals are also possibilities, for example, magnesium, lithium is the lightest of the possibilities and hence produces the greatest specific energy. It is a liquid at Venus temperature.

B. Proposed Battery

The proposed battery for Venus uses the lithium reaction with carbon dioxide to form lithium carbonate, using a molten-salt eutectic electrolyte [37]. To minimize the mass, metallic lithium is the only reactant brought from Earth.

The reaction series is

$$\text{Anode}: 2Li \rightarrow 2Li^+ + 2e^-$$

$$\text{Cathode}: 2CO_2 + 2e^- \rightarrow CO_3^{-2} + CO$$

$$\text{Overall}: 2Li + 2CO_2 \rightarrow Li_2CO_3 + CO$$

The calculated voltage produced in this reaction series [38] is 1.14 V. In addition to this primary reaction, a secondary reaction is also possible, further reducing the CO to carbon:

$$2Li + 3CO \rightarrow Li_2CO_3 + 2C$$

Adding the secondary reaction yields a net reaction of

$$4Li + 3CO_2 \rightarrow 2Li_2CO_3 + C$$

As noted in Sec. IV.C, a mixture of Li, Na, and K may be more desirable than pure Li as the anode material.

Figure 4 shows the battery in schematic. Note that lithium (density 0.51) is considerably lighter than the molten-carbonate electrolyte (e.g., Li_2CO_3, density 2.11), and so the lithium will inherently float on top of the electrolyte. The negative (cathode) terminal of the battery is an electrical connection to the electrolyte melt; the positive (anode) terminal is a direct contact to the metallic lithium.

At the cathode, carbon dioxide at 90 bar of pressure will be electrolytically dissociated into carbonate ion and carbon monoxide. Hagedorn [37] notes that this process occurs most efficiently if a catalyst (such as perovskites, pyrochlores, gold, or platinum) is

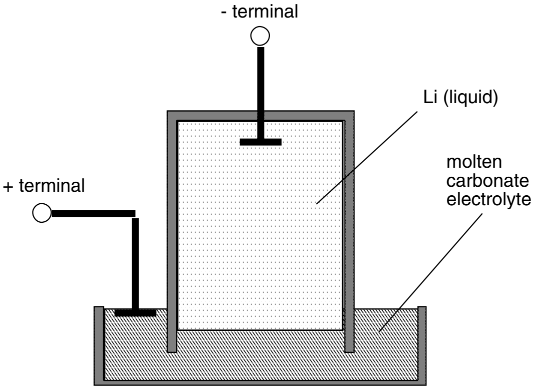

Fig. 4 Schematic diagram of proposed lithium/lithium–carbonate battery with molten-carbonate electrolyte.

present. The cathode must be open to the atmosphere, or at least be covered with a gas-permeable grid.

The diagram shown should be considered schematic, not indicative; many variant geometries are possible.

C. Electrolyte

For the operation at Venus ambient temperature, a molten salt is used for an electrolyte. The obvious choices are either halide salts or carbonate salts.

The optimum electrolyte would be a molten carbonate. This makes the battery structure very much an analog to the molten-carbonate fuel cell, and much of the technology development for molten-carbonate fuel cells will be directly applicable. This is a device structure that has undergone considerable technology development for terrestrial applications.

Although pure lithium carbonate, with a melting point of 723°C, is not liquid at Venus temperature, a eutectic mixed carbonate is. The ternary eutectic $(Li_{0.44}Na_{0.30}K_{0.26})_2CO_3$ has a melting point of 393°C [38,39], low enough to be liquid at Venus surface temperatures at all locations across the planet.

The reaction product, lithium carbonate, has a melt temperature of 723° C and, hence, is a solid at Venus ambient conditions. It will, however, dissolve in the carbonate melt. As the reaction proceeds, the volume of the lithium reactant will gradually decrease, and the volume of carbonate will gradually increase. At some point the concentration of Li_2CO_3 will become high enough for it to precipitate out from the electrolyte. Because lithium ions are more mobile than carbonate ions, it is expected that the $LiCO_3$ will precipitate primarily at the anode, and the precipitate will tend to float on the surface. A layer of Li_2CO_3 would increase the battery resistance and could impede the flow of carbon dioxide into the cell, but at the temperatures of interest, the impedance to both CO_2 and electrons is likely to be relatively low and, hence, may not present a problem.

If the buildup of Li_2CO_3 is likely to be a problem, though, the anode material itself could be a mixture of Li, K, and Na in a proportion that would produce a mixed salt that is liquid at operating temperature. In this case, the oxidation reaction at the anode would produce more of the electrolyte. [Use of a mixed-metal anode of eutectic stoichiometry would reduce the maximum possible specific power by a factor of 3, in that the average molecular mass of the reactant $(Li_{0.44}Na_{0.30}K_{0.26})$ is 20.1, and the electrochemical potential is slightly lower, 2.9 V.]

An alternate electrolyte would be a chloride salt. A chloride electrolyte would be similar to those used for thermal batteries [12]. In this mixture, the Li ion will be mobile. The detailed operation of the battery would depend on the solubility of the reaction product, lithium carbonate, in the electrolyte. If the carbonate reaction product is not significantly soluble in these salts, the production of lithium carbonate would be done entirely at the cathode. A eutectic mixture of lithium chloride and potassium chloride, with a melt point of 352°C, could be used as the electrolyte. This has been demonstrated in electrolysis cells operated at 400–500°C.

Another salt possibility is a mixture of lithium fluoride, lithium chloride, and lithium bromide in a eutectic mixture, or the quaternary salt lithium fluoride–lithium chloride–lithium bromide–lithium sulfate, melting in the range of 399–435°C, also used for thermal batteries [40,41]. By using only lithium as the cation, operation of the battery will not build up excess Li concentration in the salt, changing the composition away from the eutectic.

D. Solid Electrolyte

The concept for the battery as shown in Fig. 4 shows the lithium metal directly in contact with the electrolyte; however, another possible structure would be for them to be separated by a solid electrolyte of a material in which the lithium ion has high mobility at Venus temperature. Such material would be similar to the beta-alumina material [27] discussed in Sec. III.A. If the solubility of carbon dioxide in the molten-salt electrolyte is high enough that it reacts directly with the lithium to result in self-discharge, the use of a solid-electrolyte separator would eliminate this reaction pathway.

E. Electrochemistry

The possible half-reactions associated with the reaction for lithium carbonate are [38]

$$\text{Half-reaction 1: } 2CO_2 + 2e^- \rightarrow 2CO_2^{2-}$$

$$\text{Half-reaction 2: } 2CO_2 \rightarrow CO + CO_3^{2-}$$

Reactions 1 and 2 combined yield the production of carbonate from carbon dioxide: $2CO_2 + 2e^- \rightarrow CO + CO_3^{2-}$ $V^o = -1.91$ corresponds at $t = 0$ for a cathodic process and $V^o = 0.42$ at $t = 0$ for an anodic process [38].

The lithium half-reaction involves the oxidation of lithium:

$$\text{Half-reaction 3: } Li^+ + e^- \rightarrow Li(V^o = -3.05)$$

The balanced full reaction is $2Li + 2CO_2 \rightarrow CO + Li_2CO_3$.

As noted earlier, the carbon monoxide produced can be further reduced to carbon.

The energy released ΔH and the Gibbs free energy ΔG describe the thermodynamics of the reaction. Three possible reactions were analyzed, using thermodynamic data from [1]:

$$\text{Reaction 1: } 2Li + 2CO_2 \rightarrow Li_2CO_3 + CO$$

$$\text{Reaction 2: } 2Li + CO_2 \rightarrow Li_2O + CO$$

$$\text{Reaction 3: } 4Li + 3CO_2 \rightarrow 2Li_2CO_3 + C$$

Energetics calculations show that reaction 3, reducing the one carbon dioxide all the way to carbon, is slightly thermodynamically favored over reaction 1, whereas both are favorable compared to reaction 2. It is expected that reactions 3 and 1 would likely both take place. The relative rate of the two reactions would depend on the relative rate at which the reaction product CO diffuses away compared to the rate at which CO_2 diffuses in.

From the energetics calculation, the maximum energy produced by the battery can be derived. Because lithium is the only reactant brought from Earth, a theoretical maximum is the energy produced per unit of lithium. The calculated specific energy is 4.4 kW · h per kilogram of lithium reactant.

For a real battery, the actual specific energy must include the mass of the container, electrodes, electrolyte, and other elements of the system, as well as energy losses in the reaction. This will be considerably less than this theoretical limit.

V. Conclusions

Venus presents a harsh environment for the operation of a spacecraft, yet several choices of possible battery technology exist that could operate efficiently at the required temperature. Three well-developed battery chemistries have the possibility of operating at Venus temperature: thermal batteries, sodium–sulfur batteries, and sodium–metal chloride batteries. Of these, both thermal batteries and sodium–sulfur batteries are at or near flight-qualification readiness for aerospace applications. The sodium–sulfur battery is suggested as a choice, because it can operate under Venus ambient conditions, has a high specific energy, a low self-discharge rate, and has been demonstrated in space. The two companies that currently produce sodium–sulfur batteries are doing so at a similar specific energy. A new battery type, lithium/lithium carbonate, is proposed as a future primary-battery technology that could be developed for Venus applications, which would use the ambient atmosphere of Venus as an oxidizer. This could potentially allow an extremely high specific power.

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