Development of High Energy Density Lithium-Oxygen Reserve Batteries with Integrated Chemical Oxygen Generation

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Abstract

Some smart munitions require that reserve batteries operate multiple days after activation in a low power sleep mode, while providing multiple high-power pulses. This operational profile requires batteries with energy and power densities beyond the limits of the current liquid reserve batteries. Therefore, there is an urgent need to find the next generation of high energy density reserve battery systems that can meet these operational targets. Wasatch Ionics and Omnitek Partners, in collaboration with Brigham Young University, are developing the next generation reserve batteries based on high energy density lithium-oxygen chemistry with integrated chemical oxygen generation (COG). Lithium-oxygen batteries offer the highest known theoretical energy density of all existing lithium metal batteries. Our novel high surface area/high mesopore volume fraction oxygen cathode electrode maximizes discharge capacity by providing a large storage capacity for lithium peroxide, while enhancing oxygen diffusion and electrolyte wetting. The use of internally generated high pure oxygen enables the fabrication of a self-contained and hermetically sealed battery design, therefore, eliminating the adverse effects of moisture, nitrogen, and carbon dioxide, which are present in batteries, where oxygen is sourced from air. The result of this innovation is a novel oxygen activated reserve battery that is expected to deliver a 10-fold increase in energy density, as compared today's lithium thionyl chloride liquid reserve batteries. The main objective of the research work is to demonstrate the technical feasibility of our Li-O2 reserve battery technology by fabricating and testing functional prototypes that can meet the energy density requirements of the application. The implementation of our novel primary reserve high energy density Li-O2 batteries offers multiple advantages that address the limitations of today's lithium thionyl chloride liquid reserve batteries. The resulting product will be the development of a new type of reserve battery with significantly higher energy density, faster activation time, and lower cost than the existing liquid reserve batteries. As part of this effort, we are also developing metal-oxygen batteries with stored compressed oxygen that can be used as reserve and primary batteries.

Keywords
Reserve batteries; lithium-oxygen batteries; oxygen chemical generation; on-demand activation/deactivation.

Introduction

Single use reserve batteries for military applications range from ordinance guidance systems to torpedoes, smart ammunition, mines, sonobuoys, unattended ground sensors, UAVs, artillery fuses, and many others [1]. These types of batteries must be able to operate in the harshest outdoor environments over a wide temperature range (-55°C to 125°C); they must be ready on very short notice with activation times of less than 100 ms; and must have extremely long shelf lives (>20 years). Thermal batteries and liquid reserve batteries have generally filled these requirements. However, while the military systems are becoming more sophisticated and miniaturized, the reserve battery technologies used to power them have remained essentially unchanged for decades. Traditional primary liquid reserve batteries rely on the lithium thionyl chloride (Li-$SOCl_2$) chemistry. In these types of batteries, thionyl chloride ($SOCl_2$) serves both as the cathode active material and the electrolyte. The battery is activated when the liquid electrolyte enters in contact with the lithium metal anode. Although Li-$SOCl_2$ batteries have an impressive theoretical energy density of 1,470 Wh/kg, high operating voltage (>3V), and decent discharge rate capability, practical reserve configurations can only deliver a small fraction of this value. This is mainly caused by the need to store the toxic and corrosive thionyl chloride liquid electrolyte, separately from the rest of the battery, inside a bulky liquid ampoule that needs to be ruptured during the activation step.

The new Bottom Attach munitions for the Close Terrain-Shaping Obstacles (CTSO) program, currently under development by the Army, requires that reserve batteries operate 30 days after activation in a low power sleep mode, while providing multiple high-power pulses. This

operational profile requires batteries with energy and power densities beyond the limits of the current reserve batteries. Therefore, the Army has an urgent need to find the next generation of high energy density reserve battery systems that can meet these operational targets.

After decades of basic and applied research efforts dedicated to the development of rechargeable lithium-oxygen batteries (LOBs), they have become one of the most promising lithium metal chemistries. In their simplest configuration LOBs consist of an active porous carbon electrode, as the cathode material, a lithium metal anode with a separator, and an organic electrolyte in between (Figure 1). During the discharge process, lithium metal in the anode is oxidized to lithium ions (Li^+), which migrate through the liquid electrolyte and across the separator to the carbon cathode electrode. At the same time, oxygen accepts electrons from the external electrical circuit, and it combines with Li^+ to form the solid discharge products (mostly lithium peroxide, Li_2O_2) on the active sites of the porous cathode carbon electrode. During the battery charging step, the electrochemical process is reversed, and lithium peroxide is converted back to lithium metal and oxygen gas. The oxidation of lithium to lithium peroxide is a two electron exchange reaction. The underlying electrochemical reactions are:

Anode Reaction: $2\ Li \leftrightarrow 2\ Li^+ + 2e^-$
Cathode Reaction: $2\ Li^+ + O_2 + 2e^- \leftrightarrow Li_2O_2$
Overall: $2\ Li + O_2 \leftrightarrow Li_2O_2$ (E_{OCV}=2.96 V vs. Li/Li^+)

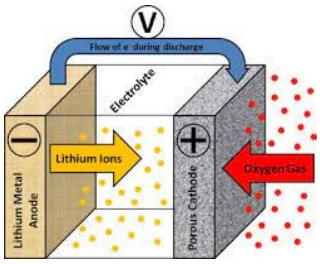

Figure 1. Li-O_2 battery

Although, the thermodynamic open cell voltage (OCV) of 2.96V is comparably low to other lithium battery chemistries, such as lithium-ion or lithium thionyl chloride, lithium-oxygen has the highest theoretical specific mass and volumetric energy densities of all the lithium batteries.

Despite the considerable energy density advantage, LOBs also face several challenges, derived mainly from the solid and insulative discharge product (Li_2O_2), the sluggish oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) kinetics, and the strong oxidative environment encountered during the charging step. These issues result in: (1) poor rate capacity due to clogging and deactivation of the active cathode electrode sites, (2) a large overpotential (>1V) during charging, which results in low coulombic efficiency, and (3) low cycling life.

In the last decade, there has been significant progress in the formulation of new porous cathode electrode materials that maximize the solid Li_2O_2 storage capacity. In addition, the incorporation of novel ORR and OER catalysts into the oxygen cathode structure, and the use of solid-state electrolytes, has substantially reduced the charge overpotential and improved the cycling ability of the batteries.

Our Innovation

Wasatch Ionics and Omnitek Partners have been working on the development of the next-generation reserve batteries based on high-energy-density lithium-oxygen chemistry with integrated chemical oxygen generation (COG).

Our novel high surface area/high mesopore volume fraction oxygen cathode electrode maximizes battery discharge capacity by providing a very large storage capacity for lithium peroxide (Li_2O_2), while enhancing oxygen diffusion and liquid electrolyte wetting. The use of internally generated high-purity oxygen enables a self-contained and hermetically sealed battery design, therefore, eliminating the adverse effects of moisture, nitrogen, and carbon dioxide, which are present in batteries where oxygen is sourced from air. The result of this innovation is a reserve battery that delivers a significant improvement in energy density, as compared to all of today's commercial lithium thionyl chloride liquid reserve batteries. Figure 2 compares the actual energy and power

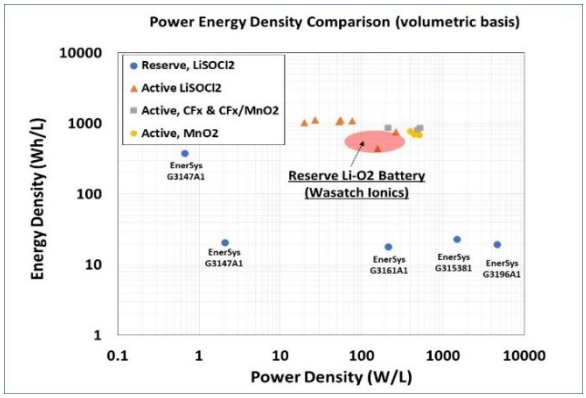

Figure 2. Comparison of energy density (Wh/l) vs. power density (W/L) for commercial lithium thionyl chloride, CFx, and MnO_2 liquid reserve and active batteries vs. Wasatch Ionic's O_2 activated reserved Li-O2 battery with integrated chemical oxygen generation.

densities of our reserve O_2-activated LOB, with integrated chemical oxygen generation, against several existing commercial liquid reserve and active batteries. The improvement is very significant when compared to commercial liquid reserve lithium thionyl chloride batteries, and it can even match the energy density performance of active CFx and $LiSOCl_2$ batteries.

Chemical Generation of High Pure Oxygen

An alkaline metal chlorate-based chemical oxygen generation (COG) system is integrated inside the reserve LOB to supply high-purity pressurized oxygen to the battery during discharge. The battery can remain inactive

for many years, and then be quickly activated on-demand by this generation capability. COG by thermal decomposition of alkali metal chlorates and perchlorates is a mature and safe technology used for emergency oxygen supply in mines, submarines, and airplanes. The many advantages of COG include:

1. **Supply of pure oxygen without battery damaging contaminants.** Traditional lithium-air batteries suffer from deactivation and poor electrochemical efficiency caused by the presence of air contaminants. The lithium metal anode reacts very energetically with water and nitrogen, and CO_2 can interfere with the formation of a stable protective solid electrolyte interface layer (SEI) on the anode surface. By comparison, thermal decomposition of chlorates generates a very pure stream of oxygen gas, free of those contaminants.
2. **On-demand generation of pressurized oxygen.** The rate of oxygen generation by the thermal decomposition of chlorates is independent of the oxygen pressure [10]. Hence, oxygen can be pressurized inside the battery casing without affecting its rate of production. The use of oxygen chlorate candles is a much more efficient long-term O_2 storage method since the reactants occupy less volume (for any oxygen pressure less than 4000 psi). The method also prevents undesirable leaks or safety issues derived from long-term storage of high-pressure oxygen.
3. **Fast activation and preheating of the battery active material.** As opposed to the standard liquid reserve batteries, wherein the release of an externally stored liquid electrolyte activates the battery, metal-oxygen batteries are activated by the diffusion of oxygen gas into the porous cathode electrode. In a reserve LOB, the liquid electrolyte is added to the battery during assembly. This ensures that the electrolyte is already uniformly distributed and wetted by all the porous surfaces within the battery by the time of activation. It is well known that gases diffuse much faster than liquids. Therefore, reserve LOBs can be activated much faster than liquid reserve batteries. Another advantage of LOBs with integrated chemical oxygen generation is that the produced oxygen will be above ambient temperature due to the heat released during the thermal decomposition of the chlorates. As a result, the gas can help to quickly preheat the battery. This is a key advantage for reserve batteries that need to be stored and/or are operated in very cold environments and activated very quickly.

On-Demand Reserve Battery Activation/Deactivation

Currently available reserve batteries cannot be turned off or deactivated once they have been activated. However, to extend their operational time, it is highly desirable that reserve batteries can be partially or completely deactivated in times of low power or no-power periods, and similarly be reactivated to their full power capacity when the external power requirements increase. Figure 3 illustrates a conceptual design of a LOB, with integrated chemical oxygen generation, that can be activated and deactivated on demand. Driven by a prescribed acceleration profile, an inertial igniter initiates the first COG unit, which fills the gas storage compartment with oxygen. A normally closed O_2 flow control valve allows enough oxygen to flow into the battery's core to activate the LOB, which can now power the device and operate a linear solenoid to actuate the oxygen flow control valve from that point on. The flow control valve would open when more oxygen is required by the LOB to keep supplying electric power to the external load, or close to deactivate the battery in no-power periods. Additional COG units can be added to the reserve battery to increase the amount of oxygen. These additional COG units can be activated on demand by powering an electrical initiator. Alternatively, or in combination, the reserve

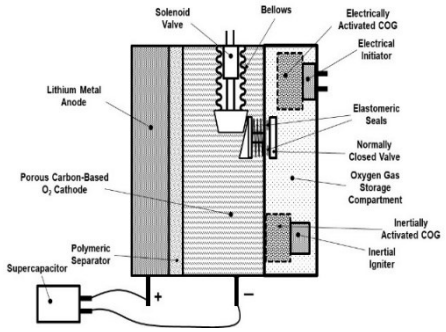

Figure 3. Conceptual design of a LOB with integrated chemical oxygen generation that can be activated and deactivated on demand.

battery can also be fitted with a supercapacitor that is charged from the LOB. The energy stored in the supercapacitor can be used, for instance, to provide high power pulses to external loads. In summary, our concept provides a lot of flexibility in terms of how the reserve battery can be used, while it significantly extends the on-line operational time.

Acknowledgements

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