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RESEARCH NOTE

Sea Water Activated Magnesium-Air Reserve Batteries: Calculation of Specific Energy and Energy Density for Various Cell Geometries

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ABSTRACT:

We address sustainable energy issues via scrutinizing magnesium-air reserve batteries. Such energy storage systems can hold their energy indefinitely, releasing it on demand, in emergency situations. Main advantage of water-activated batteries is that their electrolyte is supplied by the environment, where they get deployed, hence, only light weight electrodes and battery frames should be transported, rather than the significantly heavier aqueous electrolyte. Recent literature in the field is reviewed. One merit of this account is that recently, battery storage has become an effective way to increase share of renewables in photovoltaic energy systems utilized in farming. While the specific energy of reserve batteries can be determined unequivocally, their energy density calculation needs a clear definition of the considered battery volume. Therefore, this paper proposes a new modality of evaluating specific energy and energy density of seawater-activated metal-air reserve batteries for prismatic and cylindrical geometries, respectively. Author(s) stated no compete of interest.

1. Background

The "urban century" has arrived in which we have to address a broad suite of sustainability challenges in both urban (Elmqvist et al., 2019) and rural areas. The need for electricity generation is continuously increasing in modern societies. One main goal of global energy sustainability is to replace the fossil fuel- based energy by renewable energy and reduce emissions (Lachuriya and Kulkarni, 2017). Governments, companies and academics worldwide are becoming increasingly aware of the renewable and sustainable energy transition (Reid *et al.*, 2010; Marcucci and Turton, 2015). This is supported, among others by the Framework Strategy for a Resilient Energy Union, in which the European Union has highlighted its energy priorities for transition to a low-carbon, secure and competitive economy (Kougias et al., 2019). Recently, battery storage has been emphasized as an effective way to increase share of renewables in photovoltaic energy systems utilized in farming (Lane *et al.*, 2019). Here we address reserve batteries or deferred-action batteries, which are primary cells intended for emergency use. Also called stand-by batteries, they do not source power until activated. To avoid self-discharge, the electrolyte is kept separately from the electrodes, which remain in dry inactive state. As a result, they retain their charge during long storage periods, during which the active materials do not degrade over conventional storage, withstand deterioration and, ultimately, self-discharge of batteries prior to their activation is eliminated. Hence, reserve batteries possess a quasi-unlimited shelf life, which is often referred to as an “infinite” shelf life. They are activated on demand, by introducing the electrolyte into the cell. Allowing the access of the electrolyte between the electrodes, establishes the internal (ionic) circuit of the cell, and a reserve battery gets activated, delivering power almost instantaneously (Abdul−Zehra, H., 2018.) Types of reserve batteries include the ones based on the movement of electrolyte (sea water, energizers, and reserve silver-zinc, or lithium-thionyl chloride cells) and thermal batteries, which are activated at high-temperature (Ritchie and Bagshaw, 1996.) Reserve batteries belong to several groups listed below.

1.1 Ampoule batteries, in which the electrolyte is stored in a separate container, located in the battery case; the

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battery is activated by breaking the ampoule, which enables the dispensing of the electrolyte into the cell. One example is the spin-activated lead-acid reserve battery, which discharges in about 4 minutes, being used extensively in artillery, for powering electronic fuses and sensors. Its typical electrolyte is fluoroboric acid. When the ampoule containing the electrolyte is opened by a rotary cutter or crushed by a weight, the electrolyte wets the cell stack by the centrifugal force of the shell spinning. Full voltage is normally reached within a few tens of milliseconds. The battery usually consists of a stack of bipolar electrodes, when high voltage is needed, or is equipped with a set of alternate anodes and cathodes connected in parallel to source high current.

1.2 Thermal batteries are primary reserve batteries that are solid state at normal temperature. They contain a solid electrolyte (typically a mixture of lithium chloride and potassium chloride), which is dormant at ambient temperatures, and melts, i.e., becomes active upon heating, by using an internal pyrotechnic. So, the operation of thermal batteries is triggered by heat from an external source, which melts the electrolyte.

1.3 Gas-activated batteries are being started by introducing a gas into the battery system. This gas can be either the cathode-active material or part of the electrolyte. Historically, gas-activated batteries offered the potential of a simple and helpful means of activation. Given that gas is nonconductive, it could be distributed through a multicell assembly without posing the risk of short-circuiting the battery. Nevertheless, gas-activated batteries are no longer in production, because other systems have more advantageous characteristics (Abdul−Zehra, H., 2018.)

1.4 Spin-dependent or spin-activated reserve batteries contain a stack of bipolar electrodes, when high voltage is needed, or a set of alternate anodes and cathodes connected in parallel to source high current. They offer a long shelf life and high performance at low temperatures. Ambient-temperature lithium anode reserve batteries belong to three major types: (i) lithium/vanadium pentoxide, (ii) lithium/thionyl chloride, and (iii) lithium/sulfur dioxide batteries (Reserve Battery Information, 2019.) Among the advantages of high-power lithium primary reserve batteries, one should mention a wide temperature range (from -40 to +80 ℃) and up to 20 years of storage life, with self-discharge of 1% per year at room temperature (Tadiran Batteries, 2019.)

1.5 Water-activated batteries using seawater or some other water (brackish water or wastewater) as the electrolyte. This electrolyte is supplied by the surroundings of the battery, when the cell is deployed. This kind of operation offers the advantage of not having to transport along with the cell any heavy electrolyte (Clark, Latz, and Horstmann, 2018). Typically, a large variety of aqueous solutions can be used in water-activated reserve batteries, which are specifically designed to pollute less, as they use either limited amounts of heavy metals or are completely free of heavy metals. Some advantages of water-activated batteries are their reliability, safety in operation, light weight (without the electrolyte), high power density, elevated specific energy, instantaneous activation, and infinite shelf life. Also, they are cost-effective and do not need maintenance. Owing to their special design, these cells pollute less, being considered environmentally friendly, as they use less or no heavy metals. Among the few shortcomings of water-activated batteries one should mention that after activation they undergo fast self-discharge, and once activated, they operate as primary cells, so upon running out of power, they need to be replaced. A high-energy seawater-activated system is the primary magnesium-silver chloride battery, which offers extraordinary reliability and performance. They can be stored indefinitely, in a wide variety of conditions, with insignificant degradation of performance. Given that magnesium-silver chloride batteries activate instantly at any temperature and depth in the ocean, they can power sonobuoys, and survival gears. Aluminum-silver oxide seawater batteries (Al/AgO) are under development and may offer power densities up to 1.20 kW kg^{-1} and energy densities of 250 Wh kg^{-1} (Reserve Batteries, 2018.) Typical representatives of water-activated batteries are metal-air cells, which represent important power sources for various applications, owing to their high theoretical energy density and low cost. Such batteries operate with a metal anode and an air-breathing cathode via a suitable electrolyte (Clark, Latz, and Horstmann, 2018.) The open configuration of metal-air batteries allows the air (oxygen being the oxidizing agent) to be acquired directly from the surroundings, instead of the prior incorporation of any other oxidizing agent. Not having an oxidizing agent included in the system lowers the overall mass of the cell and by this contributes to the very high theoretical energy density of metal-air batteries. Among various types of metal-air batteries significant attention has been paid to lithium-air and zinc-air batteries (Bruce *et al.*, 2012.; Girishkumar *et al.*, 2012.; Sapkota and Kim, 2009.; Lee *et al.*, 2011.), while magnesium-air batteries have been explored to a lesser extent. In the latter category cells are equipped with anode materials consisting of metallic Mg or Mg alloys, such as AZ31 or AZ61 (Feliu Jr. *et al.*, 2014.) and an efficient air cathode catalyst were identified (Zhang, Tao and Chen, 2014). Electrodes made of AZ31 magnesium

Table 1: Specifications of the customary metal-air batteries (based on References: Reserve Batteries, 2018.; Clark, Latz and Horstmann, 2018.; Bruce *et al*., 2012.; Girishkumar *et al*., 2012.; Sapkota and Kim, 2009.; Lee *et al*., 2011.)

Battery	**Cell voltage** (theoretical, V)	**Specific capacity** (theoretical, Ah kg^{-1})	**Specific energy** (theoretical, kWh kg^{-1})	**Cell voltage** (nominal, V)
Li–air	2.91–3.40	1170	13.0	2.4
Zn–air	1.60–1.65	658	1.3	1.0–1.2
Mg–air	3.1	920	6.8	1.2–1.4
Na–air	2.3	687	1.6	2.3
Al–air	2.7	1030	8.1	1.2–1.6

alloys were manufactured by twin roll strip casting and rolling (Oktay and Ürgen, 2015.)

As demonstrated by potentiodynamic polarization tests and electrochemical impedance spectroscopy twins enhance the electrochemical activity of the AZ31 alloys. Intermittent discharge tests performed with an AZ31 Mg alloy – air battery with twins had remarkable discharge behavior, such as a higher discharge voltage and a shorter retardation time than with pure metallic Mg anodes (Huang *et al*., 2013.)

Aluminum can also be utilized as the anode, as it offers one of the highest theoretical energy densities of all batteries. Nevertheless, they are not widely used because of high anode cost and problems related to byproduct removal, when operated with conventional electrolytes. One should consider, however, that an electric vehicle equipped with Al-air batteries has potential for up to eight times the range of a lithium-ion battery, while it weighs significantly less (Liu *et al.*, 2017.) As a recent development, rechargeable Mg–air batteries are a promising alternative to Li–air cells. They are safe, have low price originating from abundance of magnesium on the earth, and they possess high theoretical capacity, based on anode: 3832 Ah L^{-1} for Mg vs. 2062 Ah L^{-1} for Li (Li, Sun *et al*., 2017.) Use of bi-functional catalysts open new avenues toward the rechargeable Mg-air batteries, with reversible oxygen reduction and evolution reactions (Clark, Latz and Horstmann, 2018.) Nevertheless, there is a scarce literature on highly reversible Mg–air batteries. Fundamental scientific problems hinder the rapid development of secondary Mg–air cells, namely, poor thermodynamics and kinetics properties caused by the formation of MgO or MgO_2 insulating films on air–breathing cathode, over the initial discharge. This blocking oxide film contributes to the increase of the overpotential and a causes high polarization. Use of organic electrolytes and nanostructured electrodes may be able to enable an ideal reaction pathway in novel cell configurations (Zhang *et al*., 2014.), cathode improvements, such as chemically

Table 2: Specifications for prismatic reserve battery

Battery Specifications	**Unit**	**Value**
Length	[cm]	20
Width	[cm]	12
Height	[cm]	25
Volume	[L]	6.0
Mass (total)	[kg]	1.2
Mass (Magnesium anodes, Mg)	[kg]	0.8
Theoretical Capacity (from Mg)	[Ah]	882
Nominal Voltage	[V]	1.5
Theoretical Energy	[kWh]	1.32
Specific Energy*	[Wh kg-1]	1.1
Energy Density**	[Wh L-1]	0.22

* Total mass taken into calculations is the sum of masses of electrodes and battery mechanical frames; no mass of electrolyte is being added

** Total volume includes the space between the electrodes, where the electrolyte penetrates upon deploying the reserve battery

Table 3. Specifications for cylindrical reserve battery

Battery Specifications	Unit	Value
External diameter	[cm]	12
Internal diameter	[cm]	8
Height	[cm]	20
Volume (external)	[cm3]	2,262
Volume (external) - Volume (internal)	[cm3]	1,257
Theoretical Capacity (from Magnesium)	[Ah]	220
Nominal Voltage	[V]	1.5
Theoretical Energy	[Wh]	330
Energy Density (external volume, Eq. 1)	[Wh L-1]	146
Energy Density (volume difference, Eq. 2)	[Wh L-1]	263

modified open−mesoporous carbon nanofibers (Cheng, Lee et al., 2018) or conversion type cathodes (Zhang, Dong et al., 2018). Here we discuss the specific energy and energy density of seawater-activated magnesium-air batteries with prismatic and cylindrical geometry, respectively. Given this topic, it is of interest to compare the theoretical parameters of several metal-air batteries, compiled by Yisi Liu and co-workers (Liu, Sun *et al*., 2017) and Arafat Rahman and co-workers (Rahman, Wang and Wen, 2013.), and listed in Table 1. Summarized are the theoretical and nominal voltage, theoretical specific capacity, and energy density of the customary metal-air batteries. After activation, zinc, magnesium, or aluminum dissolve over time; so, they are sacrificial anodes. Cell operation ends at the time, when no more anode metal is left in the cell. Therefore, such reserve batteries are anode limited.

2. Definition and Calculation of Specific Energy and Energy Density for Reserve Batteries

These parameters can be determined in a straightforward manner for encased batteries. Nevertheless, they become more sophisticated for open cells, where a few conventions should be adopted prior to calculations. For an easy understanding we will cover in detail calculations for two geometries: prismatic and cylindrical cells. In both cases we assume that the mass of the electrolyte, typically sourced by the environment of the cell, does not add to the overall mass of the reserve battery.

2.1 Prismatic Reserve Battery

As an example of calculation, let us consider a prismatic reserve battery, with the specifications listed in Table 2 (Dornajafi *et al*., 2017.) The specific energy value reported in Table 2 does not consider the mass of the electrolyte, which is supplied by the natural environment, where the cell is being deployed. Hence, the total mass considered is the sum of masses of electrodes and the mechanical frames of the battery. By contrast, the volume used for energy density calculations includes the void space between the electrodes, where the electrolyte streams into the cell upon deployment.

2.2 Cylindrical Reserve Battery

The energy density calculations become more complicated for a pipe-shaped reserve battery (schematic shown in Figure 1), which has the anodes sandwiched in between two cylindrical cathodes. In this case, the mass of the cell can be weighed in a reliable manner, but its volume is more difficult to be delimited. The question here is, whether the volume to be considered for energy density calculation should be the total (external) volume, according to Equation 1, or the difference between the external and internal volume, as shown by Equation 2 (All parameters of the equations are defined in Figure 1.)

$$V_{external} = \pi \bullet \left(\frac{L}{2}\right)^2 \bullet H \quad (\mathbf{1})$$

$$V_{external} - V_{internal} = \pi \bullet \left(\frac{L}{2}\right)^2 \bullet H - \pi \bullet \left(\frac{l}{2}\right)^2 \bullet H \quad (\mathbf{2})$$

As an example of calculating the energy density in both assumptions, we will use data listed in Table 3. While the specific energy of the battery should be the same (given the constant mass of the reserve battery), the last entries of Table 3 reveal that the energy density is significantly different for the two volumes considered.

As revealed by Table 3, considering the volume in between the electrodes, and neglecting the innermost volume of the reserve battery, yields 1.8 times greater energy density than using the whole cell volume. The innermost empty space/room of the reserve battery may accommodate a device to be powered, i.e., the battery may be built around the device; in such scenarios Equation 2 (smaller volume considered) may be more appropriate for energy density calculations than Equation 1 (where the entire volume is used in calculations).

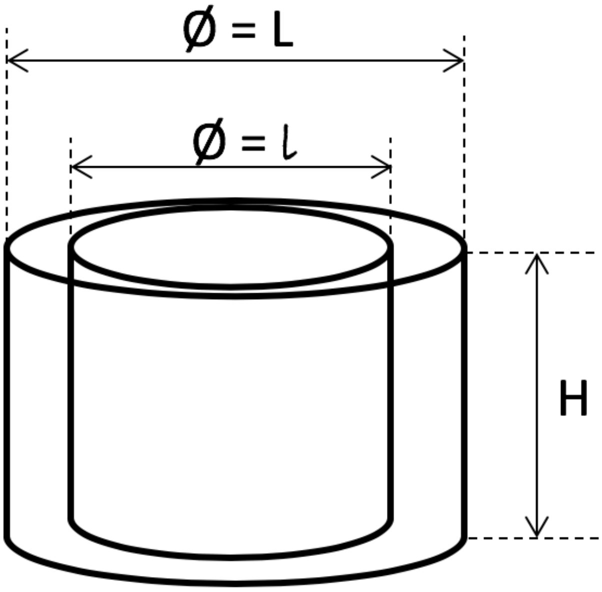

Figure 1. Schematic of the pipe-shaped reserve battery

Conclusions

Reserve batteries supply power on demand, typically in emergency situations. One example is man-overboard situation, when a passenger has fallen off the ship into the water and needs immediate rescue. When such an unfortunate event happens, the main problem is to locate the member of the crew in the water. Should the victim carry in his/her life jacket a GPS emitter or personal locator, the recovery has a much greater chance. Such electronic devices can be powered by a reserve battery, which fits into the pocket of the life vest, and gets activated instantaneously in contact with water. Other emergency applications include marine use for sonobuoys, air sea rescue equipment, emergency lighting, and weather balloons.

In addition, recently, battery storage has been emphasized as an effective way to increase share of renewables in photovoltaic energy systems utilized in farming.

The main advantage of water-activated batteries is that their electrolyte is supplied by the environment, where they get deployed; hence, only the typically light weight electrodes and battery frames need to be transported, rather than additionally carrying the aqueous electrolyte. While the specific energy of reserve batteries can be determined unambiguously, their energy density calculation needs a clear definition of the considered battery volume.

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Composition of the alloys are designated by their alphanumeric designation: AZ31 contains 3 wt.% Al and 1 wt.% Zn, while AZ61 contains 6 wt.% Al and 1 wt.% Zn, ca. 0.25 wt.% Mn, the rest of the balance being Mg.

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