Article

Overcurrent Abuse of Primary Prismatic Zinc–Air Battery Cells Studying Air Supply Effects on Performance and Safety Shut-Down

Fredrik Larsson [1,2,*], Antti Rytinki [1], Istaq Ahmed [3], Ingvar Albinsson [4] and Bengt-Erik Mellander [1]

[1] Department of Physics, Chalmers University of Technology, Kemivagen 9, SE-41296 Gothenburg, Sweden; antti.rytinki@outlook.com (A.R.); f5xrk@chalmers.se (B.-E.M.)
[2] Electronics, SP Technical Research Institute of Sweden, Brinellgatan 4, SE-50115 Borås, Sweden
[3] Volvo Group Trucks Technology, Sven Hultins gata 9, SE-41288 Gothenburg, Sweden; istaq.ahmed@volvo.com
[4] Department of Physics, University of Gothenburg, Fysikgarden 1, SE-41296 Gothenburg, Sweden; ingvar.albinsson@physics.gu.se
* Correspondence: vegan@chalmers.se or fredrik.larsson@sp.se; Tel.: +46-10-516-5000
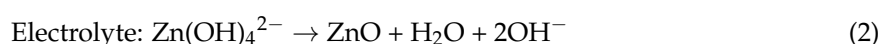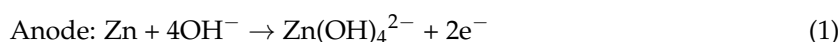
Abstract: Overcurrent abuse has been performed on commercial 48 Ah primary prismatic zinc (Zn)–Air battery cells with full air supply as well as with shut-off air supply. Compared to other battery technologies, e.g., lithium-ion batteries, metal–air batteries offer the possibility to physically stop the battery operation by stopping its air supply, thus offering an additional protection against severe battery damage in the case of, e.g., an accidental short circuit. This method may also reduce the electrical hazard in a larger battery system since, by stopping the air supply, the voltage can be brought to zero while maintaining the energy capacity of the battery. Measurements of overdischarge currents and current cut-off by suffocation have been performed to assess the safety of this type of Zn–air battery. The time to get to zero battery voltage is shown to mainly be determined by the volume of air trapped in the cell.

Keywords: abuse; air supply; metal–air; overcurrent; overdischarge; primary battery; safety; suffocation; zinc (Zn)–air

1. Introduction

New battery technologies offer power and energy densities that make it possible to construct applications with impressive performance. Lithium-ion batteries have, for example, made it possible to produce electric vehicles with reasonable range and there are expectations that the next-generation batteries such as zinc (Zn)–air, lithium–air and fuel flow batteries could provide further strides towards even more competitive products, promoting, among other things, extended electromobility in the future [1,2]. As for all new technologies, it is important to know and understand the potential risks associated with their applications. Lithium-ion batteries have, in general, a good safety record; however, the cells contain reactive materials as well as a volatile and flammable electrolyte. A so-called thermal runaway can occur in Li-ion cells, resulting in excessive heat, emission of toxic gas and eventually fire and/or explosion [3,4]. Safety aspects for lithium-ion batteries have been studied using various types of abuse tests such as overcharge, overdischarge, short circuiting, external heating and fire [5,6]. Such tests are very important in order to evaluate and minimize risks, not only for the different products using these batteries but also for the storage and transportation of the cells as well as for recycling. The risks associated with transporting lithium-ion cells by air have, for example, been a focus recently [7].

Among new developing technologies, the lithium–air battery has attracted considerable attention due to its prospected very high specific energy. The Li–air battery is still far from being commercialized and certain safety concerns are challenging [8]. In contrast to lithium-ion batteries, metal–air batteries in general may offer the possibility to limit battery reactions by stopping the air supply to the cell. One such battery type, the Zn–air battery, is promising in that the energy density is good, typically of the order of 200 Wh/kg or more, the materials used are abundant and the costs of production are expected to be comparatively low [9,10]. The battery has a hydroxide electrolyte, a Zn anode and atmospheric oxygen is reduced at the cathode. The cell is in many respects similar to a fuel cell, and electricity is produced as long as fuel, in this case Zn, and oxygen are available. The cell reactions are:

$$\text{Anode: } Zn + 4OH^- \rightarrow Zn(OH)_4{}^{2-} + 2e^- \tag{1}$$

$$\text{Electrolyte: } Zn(OH)_4{}^{2-} \rightarrow ZnO + H_2O + 2OH^- \tag{2}$$

$$\text{Cathode: } 1/2O_2 + H_2O + 2e^- \rightarrow 2OH^- \tag{3}$$

$$\text{Overall: } Zn + 1/2O_2 \rightarrow ZnO \tag{4}$$

Zn–air batteries are regarded to be very safe, and risks are commonly only associated with possible leakage of the hydroxide electrolyte and the formation of hydrogen by Zn corrosion. Early types of Zn–air batteries contained a mercury amalgam but the present generation of these batteries is mercury-free. Short circuit currents are generally expected to be low, and this should minimize risks associated with external short circuits, but traditional abuse tests on these types of cells are rare. In this study, primary Zn–air batteries were investigated regarding overcurrent and controlled air supply flow in order to evaluate risks and possibilities related to battery safety. Besides performing an overcurrent abuse test study on Zn–air batteries, the study particularly addresses suffocation as a means to stop battery reactions and thus to cause battery shutdown. For metal–air batteries this is a principal additional safety function that is not available in other battery technologies such as lead-acid, nickel–metal hydride (NiMH) and lithium-ion batteries.

2. Experimental

2.1. The Zn–Air Cell

Tests were conducted using primary (non-rechargeable) Zn–air cells as shown in Figure 1 and specified in Table 1. The cell contained 33% potassium hydroxide (KOH) electrolyte and had a Zn anode and an air cathode with nano-sized manganese (Mn) and graphite (C). The outer prismatic cell packaging material was polyethylene. The cell had 40 air holes on one side, with a diameter of about 6 mm, the total air supply area was 1130 mm^2. The cells were pre-commercial/commercial cells from QuantumSphere of type MetAir® SC Series 4.8 (QuantumSphere Inc., Santa Ana, CA, USA). Grey duct tape, shown in Figure 1, was placed between the battery pole tabs in order to avoid accidental short circuits. In Table 1, the values for the dimensions are given for the complete cell including outer plastic sealing parts; the battery pole tabs are not included. There is an air-space of about 3–4 mm beneath the cell. The volume is simply calculated by multiplying the dimensions.

This study included a total of eight cells from the same manufacturer. Four of the eight cells were of an early design version. Before this study the new design cells were stored for around 1.5 years, unfortunately with the outer transport seal opened, exposing them to ambient air. The early cell design was stored for around one additional year. However, the cells seem to still have adequate performance. The cells with early design version were used to develop and verify the test method.
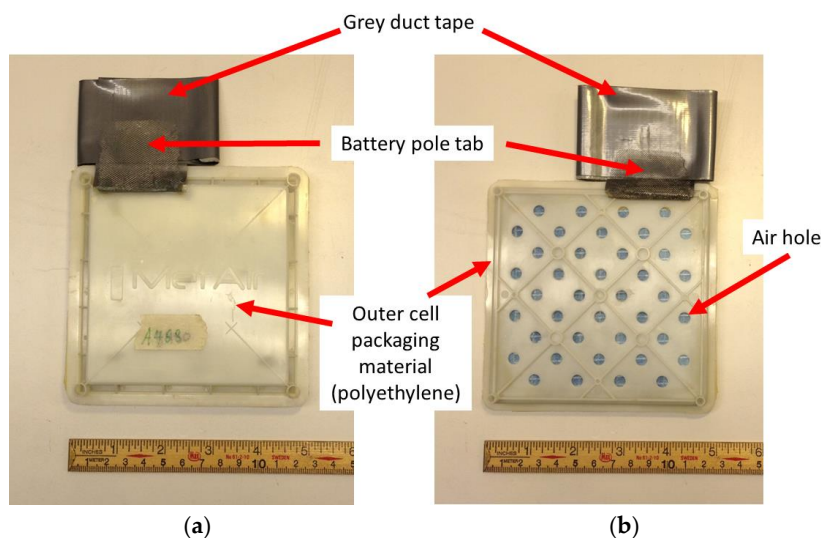
Figure 1. (**a**) Front and (**b**) back photos of the Zn–Air cell.

Table 1. Cell properties.

Parameter	Value	Unit
Nominal open circuit voltage (*OCV*)	1.4	V
Nominal voltage	1.1	V
Rated maximum continuous discharge current	4	A
Rated capacity at 1 A discharge	48	Ah
	53	Wh
Dimensions	Prismatic shape, 126 × 126 × 14	mm^3
Volume	0.22	L
Weight	270	g
Calculated energy density	196	Wh/kg

2.2. Measurement Setup

Two different experimental setups were used. One where the cell had full air supply from the surrounding air, and one where it was suffocated completely. Impedance measurements were performed in free air.

2.2.1. Open Air Setup

The cell was in this case placed inside a suffocation bag but the cell was not suffocated, see Figure 2. For open air measurements the bag was not needed but was used for consistency and to eliminate the presence of the bag as a variable. The bag itself had a square hole which fits over square air intake area of the cell. The four legs of the cell fit into four holes in the corners of the bags hole. This keeps the cell in place relative to the bag. Cable connections, using copper crocodile clamps, were placed close to the base of the cells tabs. Current wires (for discharge current) and sense wires (for cell voltage measurement) were well separated from each other. The zip lock of the bag was sealed as much as possible. The measurement cables were shielded and kept well separated to make it easy to keep an overview of the system.
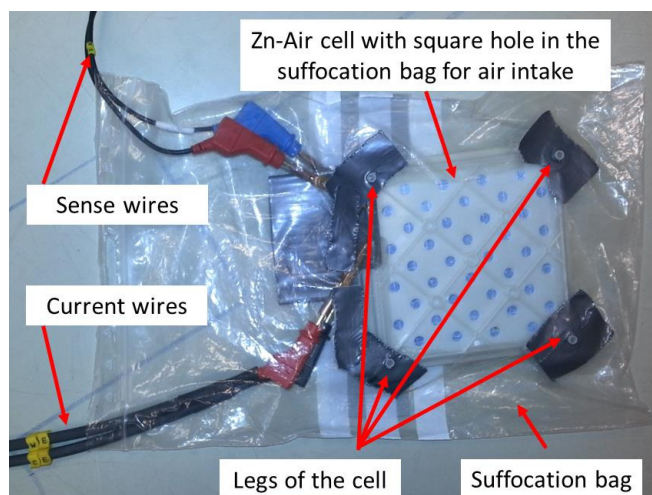
Figure 2. Open air setup, the back side of the cell with the air holes, shown in the figure, had free access to air.

2.2.2. Suffocation Setup

In addition to the steps for open air measurement, three more items were used for the suffocation setup. Figure 3a shows the suffocation plate (to the right) consisting of a square aluminum plate with a 1 cm layer of hard plastic foam followed by a layer of very soft foam, and covered in a plastic sheet (total 0.18 kg). When pressed against the air intake of the cell, the foam deformed and created a tight seal on the cell. A large aluminum heat sink (1.57 kg) and a 2.05 kg weight were placed on top of the suffocation plate so their weight made the seal tighter. When lifting the suffocation in a "first sealed, then open" experiment, all three items were lifted at once for accurate timing.
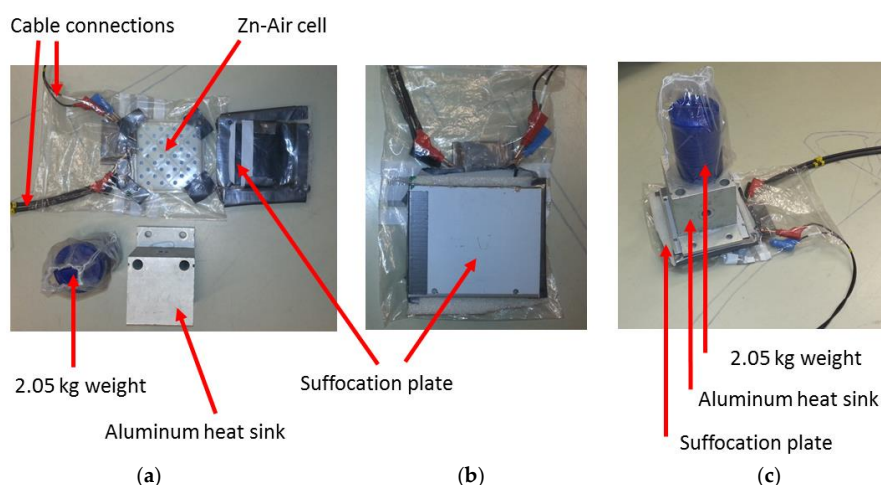

Figure 3. Suffocation setup. (**a**) All parts are separated from each other; (**b**) suffocation plate is placed over the cell; and (**c**) the aluminum heat sink and 2.05 kg weight is placed on top of the cell and suffocation plate.

2.3. Impedance Measurement

The impedance was measured using a Metrohm Autolab PGSTAT 302N (Metrohm Autolab B.V., Utrecht, The Netherlands) with Booster 20 A module (Metrohm Autolab B.V.) and Metrohm Nova 1.11 Software (Metrohm Autolab B.V.). Four-wire measurements were used, in ambient room temperature, about 20 °C, in free air, with galvanostatic mode and an amplitude of 10 mA, frequency range 10 mHz–100 kHz, with 50 points logarithmically distributed.

2.4. Discharging Measurement

The discharging measurements were also performed using the Metrohm Autolab PGSTAT 302N with a Booster 20 A module. Current and voltage were recorded at a rate of one measurement per second. The cell was orientated airside up, in order to easily control the air supply to the cell surface. The cell was placed in ambient room temperature (around 20 °C). The cell tabs were further separated by a large piece of duct tape (seen in Figures 1 and 2) attached to the cell to avoid any risk of short circuit. The bottom of the cell was sealed by the cell design; however, an additional seal composed of a plastic bag and tape was used for all the experiment performed in this study. The suffocation was applied according to the setup described in Section 2.2.2. A rest period of at least 2 h was used between two sequential discharging experiments until the open circuit voltage (*OCV*) was stabilized.

3. Results and Discussion

In all tests, a 60-s rest phase prior the start of the discharging was used for monitoring, and a longer rest phase of 900 s was used after discharging to record the recovery of the cell potential. Note that the given times in the paper are referring to the time from the start of discharge, i.e., add 60 s to the value, to correspond to the time scales in the figures.

The maximum allowed continuous discharge current of the cells is 4 A according to the manufacturer. Two types of measurements were performed. For the first type, each cell was discharged at 4 A both in open air and suffocated for 150 s or until the cell potential reached 0 V. A total of four tests were conducted for each cell, two in open air and two suffocated. In Figure 4, the results for one of the cells (cell 1) are shown. The time to reach 0 V during suffocation was 120 s. In the second type of measurement, the sealing of the cell was lifted at a pre-determined time. Also, in this type of experiment, an initial 60 s rest period was used followed by a 240 s, 4 A discharge phase where the suffocation was lifted 75 s after discharge initiation (135 s from the test start), as shown in Figure 4. These results were reproducible; repeated tests on two samples are shown in Figure 5. The experiments show that the cell recovered rapidly to the original *OCV* after suffocation, provided air access was granted. When the cell is open to air, the voltage recovers rapidly; when the cell is sealed during the whole experiment (green curve/symbols in Figure 4), the recovery is slow. The small differences shown in Figure 5 are due to minor differences regarding the voltage when the sealing was removed.
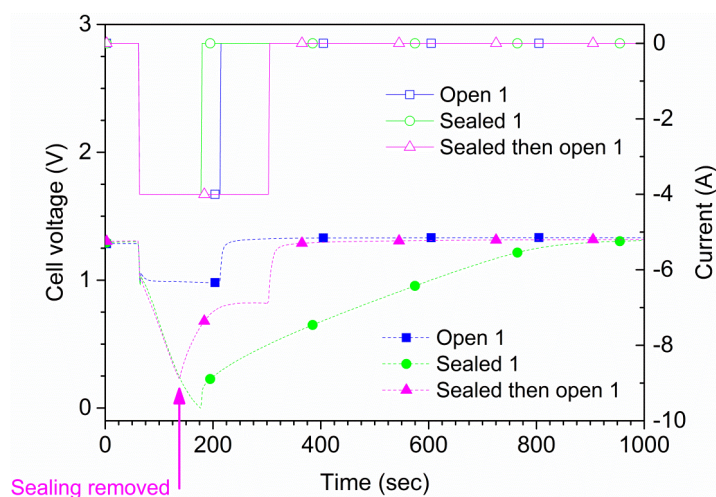

Figure 4. Voltage (filled symbols) and current (open symbols) measurements for cell 1 for three different tests using a discharge current of 4 A; in open air; sealed (suffocated) for 150 s or until the cell potential reached 0 V; and first sealed (suffocated) then open in air.
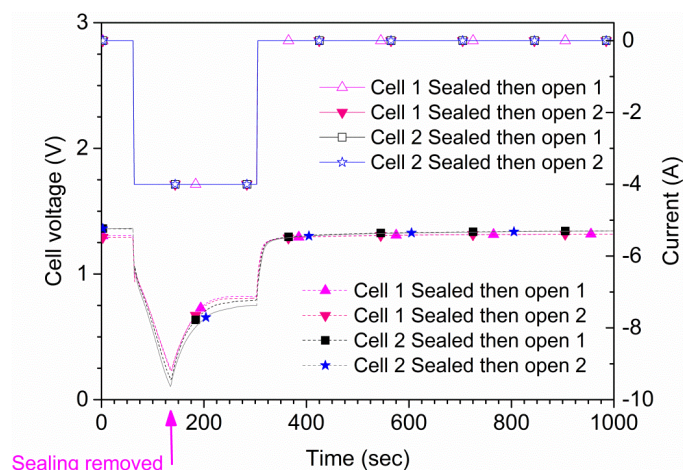
Figure 5. Voltage (filled symbols) and current (open symbols) measurements for sealed then open, for two repetitions per cell and for two different cells, cells 1 and 2.

The tests were also performed in order to find the maximum current that a cell can sustain for 2 min, as shown in Figure 6. This current was later used for maximum discharge tests. During the tests, the cell was discharged by a current of 4, 5, 6, 7, 8, 9 and 10 A for 2 min each, in this order. A cutoff triggered at 0.0 V cell potential was used, which stopped the running step and jumped to the next in case 0.0 V was reached. One of the cells showed a voltage of 76 mV at the end of the 8 A step; when changing to 10 A, the voltage rapidly reached 0 V and the test stopped. The other cell shown in Figure 6 showed a larger initial voltage drop and had a lower potential profile during the complete tests. That cell also passed the 8 A step, but not the 10 A step. Therefore, the maximum continuous current is estimated to be 8 A. This current level was used for the additional tests. Since the cells are rated for 4 A, using currents above this value is, by definition, an overcurrent. The short circuit current, I_{sc}, i.e., the current through an external conductor with negligible resistance connecting the battery pole tabs, depends on, e.g., the current path size through the battery tabs and the rate of the electrochemical reactions creating the short circuit current. I_{sc} is, in general, time-dependent (as well as dependent on various additional parameters, e.g., cell type and design, temperature, aging, state of charge (*SOC*)) and was not investigated in this study since we needed a continuous current for our measurements; the current used was therefore lower than I_{sc}.
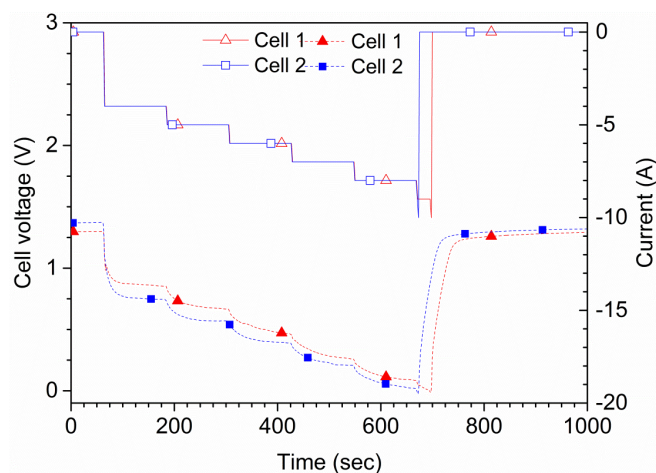

Figure 6. Voltage (filled symbols) and current (open symbols) measurements for current increment step for two different cells, cells 1 and 2.

Figure 7 shows the results for the same type of measurements as in Figure 4 but with an 8 A discharge current. With suffocation, 0.0 V was reached 36 s after the start of the discharge in the first run, and after 33 s in a second run (not shown). In open air, the cell delivered 8 A in 120 s; however, by the end of the discharge the voltage was only 14 mV. For the second run of 8 A in open air, the cell reached 0.0 V after 107 s, and did thus not reach the 120 s goal. In the sealed and open air run, the seal was removed at around 0.23 V, 27 s after the start of the discharge. The 8 A current was maintained in this case until 0.0 V was reached 135 s after the start of the discharge. A comparison between 4 A and 8 A is shown in Figure 8 for the three air supply cases.
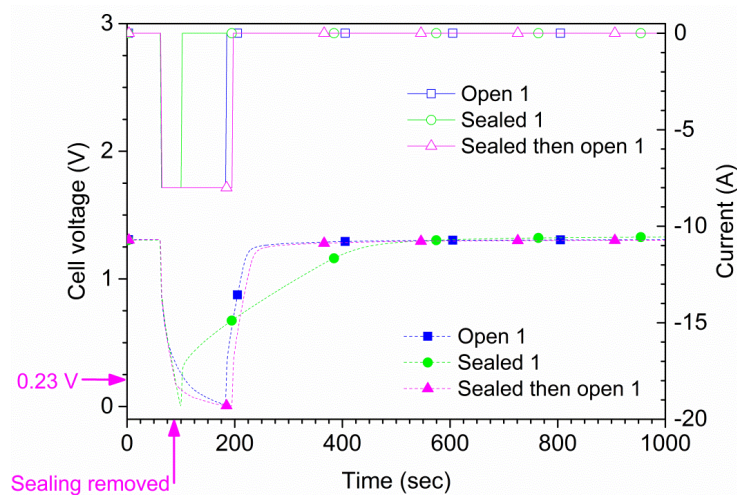

Figure 7. Voltage (filled symbols) and current (open symbols) measurements for cell 1 for three different tests using 8 A; open, sealed; and sealed then open.
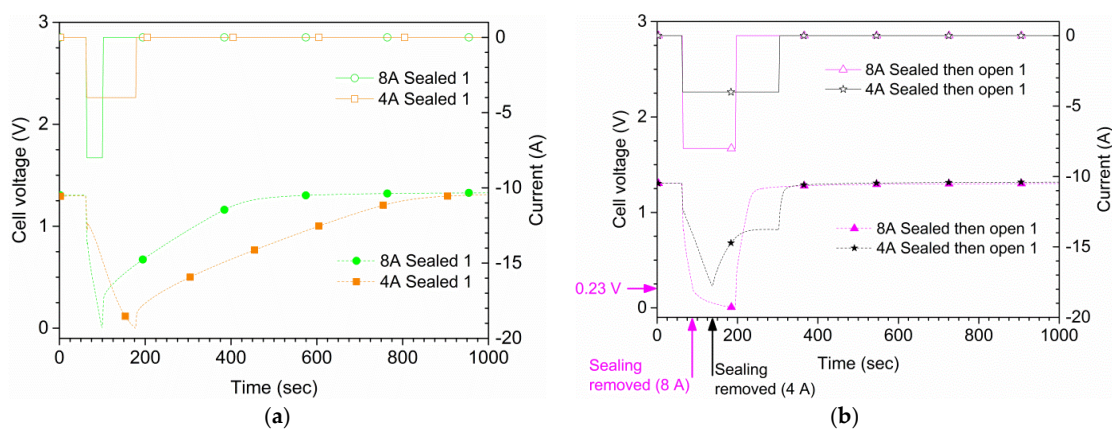

Figure 8. Voltage (filled symbols) and current (open symbols) measurements for cell 1 comparing 4 and 8 A with (**a**) sealed, and (**b**) sealed then open cell.

The suffocation experiments show that the potential of the cells rapidly goes to zero when the air supply is stopped. Starting from the cell reactions, Equations (1)–(4), our calculations show that the required air flow to the cell is 0.56 mL/s at a standard temperature and pressure, for a discharge current of 1.0 A. In the present case, for the 4 A discharge, the cell reached 0.0 V after approximately 120 s, corresponding to an air volume of 269 mL trapped inside cell. This volume is very close to the actual volume of the prismatic cell. For the 8 A overcurrent case, the suffocation resulted in a zero potential value already after 36 s, corresponding to an air volume of 161 mL. Of course, in this case the cell potential was decreasing also in open air, so the lower value is not unexpected. It should also be noted that the cell potential recovered quickly when the cells were re-exposed to air.

One of the important safety questions tested is: if the air supply at the cathode is stopped, is it possible to stop the battery operations efficiently in case of an emergency situation? The obtained results show that suffocation of the cell can indeed bring the cell potential to zero within a short period of time and stop further propagation of the internal reactions. The procedure is mainly limited by the volume of the cell packaging. The shutdown time is a function of the available air volume within the battery cell, and in the case of a battery pack also including the free air inside the battery system. For example, for a battery module/pack using a stack of Zn–air cells electrically connected in series and/or parallel, the amount of free air in the battery pack, arising from, e.g., interconnecting cell spacing, should be minimized in order for suffocation to be efficient. However, free air volumes are typically minimized anyway in order to achieve a compact battery pack size. Anyhow, some additional free air volumes might be useful and required for thermal management (cooling/heating) of the battery cells. The shutdown rate using suffocation may also be improved by lowering the available air volume by removing air from the system. In case of an emergency shutdown, the need of reducing the amount of oxygen in the free air volume can be supported by other methods, e.g., by a pump which could rapidly empty the free air volume; however, a too-fast pressure reduction could potentially harm the battery cell. The evaluation and testing of removing air by pumping was, however, not included in this study. In case of a battery pack with considerable free air space available, a shut-off air supply may result in a safe shutdown only after a relatively long time (including possible negative side-effects, e.g., additional pack heating due to ongoing cell discharging, etc.); nevertheless, a shutdown will eventually occur. Suffocation might thus be valuable also in this case as a potential passive safety shutdown method, as a complement to other shutdown techniques. There are faster ways to reach voltage shutdown, e.g., using electrical current fuses, contactors switching off and other circuit breakers. There are also internal cell safety devices for voltage shutdown, e.g., positive temperature coefficient (PTC) devices in case of an overcurrent. Furthermore, the suffocation offers an additional battery safety layer and an alternative means of battery shutdown which is not available in other battery technologies, e.g., Li-ion, NiMH and lead-acid batteries.

An additional essential safety improvement using suffocation for metal–air batteries would be the improved electrical hazard safety. The hazardous voltage in a large battery pack could, in principle, be brought to zero by using suffocation and combining it with a battery management system (BMS) controlled discharge circuit to empty the residual battery voltage. This way the battery would have its energy capacity preserved but with no hazardous voltage present. That could offer significant advantages for personal safety in manufacturing, transport, rescuing, service, maintenance etc. With an engineering design it is probably possible to make the suffocation a passive technique with autonomous safety, e.g., very valuable in a battery electric vehicle crash situation, in large battery packs used in stationary energy storage systems, in vessels, etc. The demonstrated principle of suffocation could thus be a useful safety device in future large battery packs of metal–air cells, e.g., in Li–air battery systems.

In the event of suffocation, a further complication may possibly arise due to hydrogen gas production from the corrosion of Zn:

$$Zn + 2H_2O \rightarrow Zn(OH)_2 + H_2 \tag{5}$$

The safety instruction for Zn–air batteries thus advises to always have good ventilation around the cell. Using suffocation for an emergency stop procedure is, however, not likely to cause safety problems with hydrogen production, since the suffocation will also stop the supply of humid air.

The age and *SOC* of the cell did not seem to influence the results in any substantial way. One cell (cell 1) was, after the previous discharge and overcurrent abuse, tested with 1 A discharge currents in steps of 5 Ah until 0.0 V was reached. The potential dropped significantly only close to the end of life and the internal impedance increased as the capacity was depleted. Figure 9 shows impedance measurements of the same cell during its use, at 0, 3.9 and 25.6 Ah discharge. Impedance plots of zinc–air batteries are complex but can often be described by a low-frequency part mainly related to cathode reactions, possibly also including a Warburg diffusion element, a medium-frequency part

mainly related to the anode; while the high-frequency region shows an inductive response that can be due to electrode porosity, cell geometry and electrical leads [11,12]. The impedance plots in Figure 9 show similar behavior but data are too limited to make an in-depth analysis in this case. Nevertheless, the results show that the series resistance (determined from the intersection with the real axis in the complex impedance plot) increased from about 18.3 mΩ to 28.2 mΩ at end of life (a 54% increase), and that the medium-frequency impedance increased with the increased discharge as expected as the anode is consumed. Also, the low-frequency part is affected, maybe partially as a consequence of the formation of zinc oxide as suggested by Schröder et al. [13]. It can be noted that the 25.6 Ah total discharged capacity is lower than the rated capacity (48 Ah with a 1 A discharge current); however, the cell had underwent abusive tests including higher discharge currents than 1 A, prior to the final discharge procedure with a 1 A discharge current.
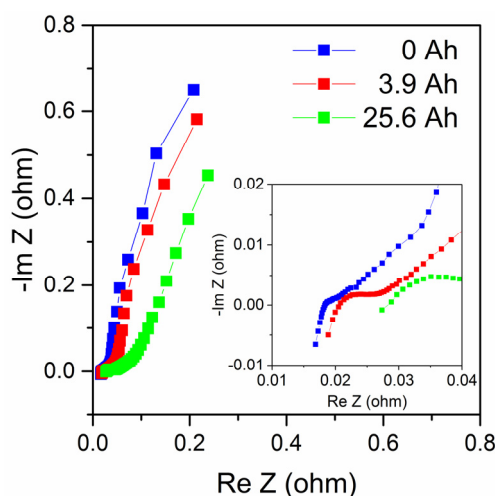

Figure 9. Impedance measurements for cell 1 showing real vs. imagined part three times: the beginning of life (0 Ah), intermediate measurement (3.9 Ah), and at the end of the testing (25.6 Ah), with a magnification around the origin in the inset.

4. Conclusions

Zn–air batteries are regarded as having a very high safety level since the possibilities for unwanted reactions are low and spontaneous reactions, e.g., as a consequence of an internal error, are unlikely. Furthermore, even if this battery technology is regarded to be very safe, interrupting the flow of air by suffocation could be a useful additional safety device, e.g., in case of internal or external short circuits or in case there is a risk of excessive temperatures, especially for larger battery systems. In this study it has been shown that suffocation may be an efficient method to bring the battery cell potential to zero and thus stop battery reactions within a short time. Using suffocation as a method to halt battery reactions may be a general possibility for batteries with an air cathode to be used in case of, e.g., internal short circuit events or external violence such as nail penetration or deformation in order to shut down a battery system. This method may also reduce the electrical hazard in a larger battery system since, by stopping the air supply, the voltage can be brought to zero while maintaining the energy capacity of the battery. As a consequence, this method may be considered also for emerging battery techniques such as the Li–air battery.

Author Contributions: Fredrik Larsson and Istaq Ahmed conceived the experiments. Fredrik Larsson designed and planned the experiments and Antti Rytinki performed the experiments. All five authors were involved in the analyses of the data and wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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