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SUPPLEMENTARY INFORMATION

Title: Lightweight Al-Mg-In Alloy Based Seawater Batteries for Long Endurance Underwater

Applications: Pack Mass and Cost Optimization

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CONTENTS

- 1. Figures, tables and calculations
- 2. References

S1. Figures



S1. Open circuit potential of 5N Al, Al3Mg, Al0.1In

Fig. S1 Open circuit potential of anodes immersed in 3.5 wt% NaCl solution for 24 h, at several temperatures. (a) 5N Al; (b) Al3Mg; (c) Al0.1In. Please note that the ordinate limits are different in the sub figures

The results show that all the anodes exhibit a more negative OCP at higher temperatures. In the case of 5N AI (Fig. S1a), the OCP increases initially, probably due to the formation of an oxide layer by the reaction between the anode and water. The OCP decrease after an hour or so can be ascribed to the breakdown of new oxide layer. The final increasing phase of OCP can be explained by a slow and continuous dissolution of the oxide and simultaneous formation of a more compact oxide layer in sea water solution. The fact that the OCP keeps changing slowly even after 24 h indicates that the process has not reached a steady state in 24 h. In the case of Al3Mg samples, the OCP values rapidly increase initially and then remain more or less a constant (Fig. S1b). At 25 and 20 °C, the OCP values of Al3Mg are at least 50 mV higher than that of 5NAl sample, whereas at 15, 10 and 5 °C, the OCP values of Al3Mg and 5NAl are only slightly different. Addition of 0.1% In to Al decreases the OCP values (Fig. S1c) to nearly -1.1 V *vs.* Ag/AgCl at all the temperatures studied.





Fig. S2 Potentiodynamic polarisation studies of (a) 5N Al; (b) Al3Mg; (c) Al0.1In in 3.5 wt% NaCl solution

The PDP results show that the samples do not passivate in 3.5 wt% NaCl solutions.

Table S2.1 Potentiodynamic polarisation values of 5N Al, Al3Mg, Al0.1In, Al3Mg0.1In

(a)

5N AI	25 °C	20 °C	15 °C	10 °C	5 °C
E _{corr} (V <i>vs.</i> Ag/AgCl)	-1.079	-1.074	-1.068	-1.06	-1.05
Corrosion current density j _{corr} (mA/cm ²)	0.0397	0.0486	0.0489	0.0287	0.0343
Corrosion rate (µm/hr)	0.0492	0.0601	0.0607	0.0356	0.0426

(b)

Al3Mg	25 °C	20 °C	15 °C	10 °C	5 °C
E _{corr} (V <i>vs.</i> Ag/AgCl)	-1.008	-0.948	-0.943	-0.896	-0.856
Corrosion current density j _{corr} (mA/cm ²)	0.0115	0.0117	0.0231	0.0121	0.0101
Corrosion rate (µm/hr)	0.0143	0.0146	0.0285	0.0151	0.0125

(c)

Al0.1In	25 °C	20 °C	15 °C	10°C	5 °C
E _{corr} (V <i>vs.</i> Ag/AgCl)	-1.107	-1.089	-1.075	-1.041	-0.995
Corrosion current density j _{corr} (mA/cm ²)	0.0417	0.0311	0.0157	0.0127	0.0113
Corrosion rate (µm/hr)	0.0517	0.0384	0.0194	0.0158	0.0141

(d)

Al3Mg0.1In	25 °C	20 °C	15 °C	10 °C	5 °C
E _{corr} (V <i>vs</i> . Ag/AgCl)	-1.274	-1.273	-1.258	-1.274	-1.23
Corrosion current density j _{corr} (mA/cm ²)	0.0626	0.0463	0.0374	0.0353	0.0285

	0.0574	0.0464	0.0437	0.0354
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In all the samples, the corrosion potential shifts in the positive direction as temperature reduces, and this is similar to the OCP trends observed. The corrosion current values of 5NAI and Al3Mg do not show a monotonic trend with temperature, but those of Al0.1In and Al3Mg0.1In show a decrease with temperature.





Fig. S3 Nyquist plots of (a) 5N Al; (b) Al3Mg; (c) Al0.1In in 3.5 wt% NaCl solution. Please note that the scales are different in the sub figures. The open makers correspond to experimental data while dashed lines corresponds to fitted data.

The Nyquist plots of EIS of 5N Al (Fig. S3a) show depressed semicircles, and are modelled using a Randles circuit without mass transfer effects. The corresponding plots of Al3Mg (Fig. S3b) show two time-constants, and are fitted using the circuit shown in the inset. The charge transfer resistance (R₁) decreases with temperature. The polarization resistance (R₁+ R₂) shows a non-monotonic trend, mainly because R₂ is estimated based on very few points, and has a large uncertainty. Nyquist plots of EIS of Al0.1In (Fig. S3c) and those of Al3Mg0.1In (Fig. 2c) were fitted to Randles circuit with Warburg impedance. In all the cases, the charge transfer resistance decreases with temperature, which is along the expected lines. The kinetics of selfcorrosion are expected to be slower at lower temperature and hence the charge transfer resistance decreases. The Warburg parameter values do not change monotonically with temperature. EIS is a very sensitive technique ¹. During anodic dissolution of metals, several processes can occur simultaneously, i.e., film formation, film dissolution and direct dissolution. In the case of alloys, the processes are even more complex, and it is very challenging to assign individual processes to the features in the EIS data. Therefore, the interpretations here are limited to employing the charge transfer resistance as an indicator of resistance to self-corrosion.

	5N AI						
	25 °C	20 °C	15 °C	10 °C	5 °C		
R _s (Ω-cm ²)	10.22	12.98	15.53	17.89	25.85		
Q-Y ₀ (F/cm ²)	2.38 × 10 ⁻⁴	1.23 × 10 ⁻⁴	1.19 × 10 ⁻⁴	2.00×10^{-4}	7.23 × 10 ⁻⁵		
Q-n	0.86	0.98	0.97	0.8	0.92		
R ₁ (Ω-cm ²)	1265	2379	3561	7506	7897		

Table S3.1 EIS fit values of 5N Al, Al3Mg, Al0.1In, Al3Mg0.1In

			Al3Mg		
	25 °C	20 °C	15 °C	10 °C	5 °C
R _s (Ω-cm²)	10.01	12.61	15.09	17.76	24.38
Q-Y ₀ (F/cm ²)	2.08 × 10 ⁻⁵	1.063 × 10 ⁻⁵	9.71 × 10 ⁻⁵	2.34 × 10 ⁻⁵	3.25 × 10 ⁻⁶
Q-n	0.83	0.93	0.93	0.91	0.93
R ₁ (Ω-cm ²)	341.15	622.3	1219	1812	2065
Q-Y ₀ (F/cm ²)	2.53 × 10⁻⁵	1.089 × 10 ⁻³	1.36 × 10 ⁻³	1.22 × 10 ⁻³	4.12 × 10 ⁻⁴
Q-n	0.91	0.83	0.99	0.92	0.75

R ₂ (Ω-cm ²)	9346	2.63 × e10	8123	6.72 × e10	5.26 × e9

			Al0.1In		
	25 °C	20 °C	15 °C	10 °C	5 °C
R _s (Ω-cm ²)	10.09	12.89	16.97	18.74	24.8
Q-Y ₀ (F/cm ²)	6.024 × 10 ⁻⁵	3.94 × 10 ⁻⁵	1.61 × 10 ⁻⁵	2.25 × 10 ⁻⁵	8.11 × 10 ⁻⁶
Q-n	0.86	0.84	0.91	0.88	0.91
R ₁ (Ω-cm ²)	270.00	453.60	765.30	1227.00	1532.00
W (Ω-cm²)	40.31 × 10 ⁻⁴	13.21 × 10 ⁻⁴	16.25 × 10 ⁻⁴	10.47 × 10 ⁻⁴	8.13 × 10 ⁻⁴

	Al3Mg0.1In						
	25 °C	20 °C	15 °C	10 °C	5 °C		
R _s (Ω-cm ²)	11.22	13.45	15.11	17.36	25.82		
Q-Y ₀ (F/cm ²)	1.27 × 10 ⁻⁴	5.99 × 10⁻⁵	7.06 × 10 ⁻⁵	3.02 × 10 ⁻⁵	2.99 × 10 ⁻⁵		
Q-n	0.71	0.67	0.70	0.80	0.66		
R ₁ (Ω-cm ²)	489.7	1229.0	1672.0	1900.0	2471		
W (Ω-cm²)	21.7 × 10 ⁻⁴	11.60×10^{-4}	11.92 × 10 ⁻⁴	9.96 × 10 ⁻⁴	5.98 × 10 ⁻⁴		





Fig. S4 Linear Sweep Voltammetry of (a) 5N Al; (b) Al3Mg; (c) Al0.1In in 3.5 wt% NaCl solution. Please note that scales are different in subplots

The LSV results show that the behavior of the anodes at 20 °C is similar to those exhibited at 25 °C (Fig. 2d). At 15, 10 and 5 °C, there is a slight difference, viz., Al3Mg alloy exhibits a more anodic potential than 5N Al at current densities exceeding 30 mA/cm², but otherwise the overall trends remain the same.

S5. Galvanostatic Discharge at 5mA/cm²



Fig. S5 Galvanostatic discharge of (a) 5N Al, (b) Al3Mg, and (c) Al0.1In with Pt/C cathode, at 5 mA/cm² in 3.5 wt% NaCl solution at 5 - 25 °C.

A comparison of Fig. S5a and b shows that addition of 3 wt% Mg improves the discharge potential at 5 mA/cm² current density, by ~ 110 mV at 25 and 20 °C, and by ~60 mV at 15, 10 and 5 °C. A comparison of Fig. S5a and c shows that the addition of 0.1 wt% In to Al largely improves the discharge potential (~ 350 to 400 mV) at 5 mA/cm² current density at all the temperatures studied.

S6. Cell Discharge Performance



Fig. S6 Cell discharge performance, i.e., I-V and I-P results of (a) 5N AI, (b) Al3Mg, and (c) Al0.1In, anode with Pt-C in 3.5 wt% NaCl solution at 5 - 25 °C. The closed markers are the cell potentials, while the open markers are the power values.

Chrono-potentiometric experiments were conducted at several other discharge current densities, and the potential values between 2 to 24 h of discharge were averaged. At a given current density, the initial potential values were higher than the average values, and hence the potentials in the first 2 hours were excluded from the calculations. The discharge curves are presented in Fig. S6 and Fig. 3c. In addition, the corresponding power values were calculated and presented in the right ordinates. A comparison of Figure S6 a and b shows that at low current densities (< 15 mA/cm²), addition of Mg to Al increases the discharge potentials at 20 and 25 °C, and decreases them at 15, 10 and 5 °C. At high current densities (> 20

mA/cm²), Mg addition degrades the performance at all the temperatures studied. When Figure S11 a and c are compared, it is clear that the addition of In to Al improves the discharge performance at all the current densities and temperatures investigated. Co-doping Mg and In (Fig. 3c) yields an intermediate discharge performance.

S7. Self-corrosion Rate



Fig. S7 Self-corrosion rate of (a) 5N Al, (b) Al3Mg, and (c) Al0.1In during battery test in 3.5 wt% NaCl solution at 5-25 °C. The markers represent the experimental results and the lines represent linear interpolations. Please note that scales are different in sub figures.

For all the samples studied, the self-corrosion rate increases with temperature and discharge current density. A comparison of Fig. S7a and b shows that addition of Mg to Al decreases the self-corrosion rate, and the effect increases at lower temperature. A comparison of Fig. S7a and c indicates that the addition of In to Al decreases the self-corrosion rate even further.

S8. Microstructure of 5N Al, Al3Mg, Al0.1In, and Al3Mg0.1In



Fig. S8 Microstructure analysis of (a) 5N Al; (b) Al3Mg; (c) Al0.1In; (d) Al3Mg0.1In using optical microscopy

Fig. S8a shows the microstructure analysis of pure (5N) Al, Al3Mg, Al0.1In, Al3Mg0.1In. Several precipitates are seen in Al3Mg and Al3Mg0.1In samples.

S9. EDAX for Microstructure grain analysis of Al3Mg0.1In

Figure S9 a and b shows the EDS analysis of the precipitates found in Al3Mg0.1In in different regions. EDS results from S5a shows that precipitates are mainly comprised of Al and Mg. Coarser precipitates comprising largely of Al, In and Fe were sparsely detected (Fig S8b).









Fig. S9 (a), and (b) Precipitate composition analysis of Al3Mg0.1In using SEM EDS



S10. XRD of pure Al, Al3Mg and Al0.1In

Fig. S10 XRD patterns of (a) 99.999% Al; (b) Al-3%Mg; (c) Al-0.1%In

The presence of α -Al phase in all the alloys is identified at 38.37°, 44.6°, 64.92°, 78.008° and 82.19° attributed to (111), (200), (220), (310) and (222) phases respectively (JCPDS 01-089-2837). Addition of Mg to Al resulted in β - Al₃Mg₂ phase (2 θ = 36.34°, 37.442°, and 65.186°; JCPDS 00-040-0903). Indium peak was matched with JCPDS 01-085-1409. Aluminum hydroxide was formed in all the samples immersed in 3.5 wt% NaCl solution (2 θ = 18.74°, 20.30°; JCPDS 01-077-0114). Impurities such as Si and Fe formed secondary compounds with Mg (2 θ = 40.126°; JCPDS 03-065-0690) and In (2 θ = 34.4°; JCPDS 01-085-2306). NaCl peak were observed at 31.76° and 45.54° (JCPDS 01-078-0751).



Fig. S11 Anode coulombic efficiency of (a) 5N Al, (b) Al3Mg, and (c) Al0.1In at 5 - 25 °C. The markers represent the experimental values and the lines represent the linear interpolations.

For pure Al, the coulombic efficiency is low (~ 66%) at 25 °C and small current densities, and it increases to about 88% at higher current densities (Fig. S11a). For Al3Mg, the coulombic efficiency is very low (~42%) at 25 °C, at 0.1 mA/cm² current density, and at large current densities, it is in the range of 85-90% at all the temperatures (Fig. S11b). For Al0.1In alloy, it is 80-90% at 0.1 mA/cm², and is in the range of 87-95% at large current densities (Fig. S11c).

S12. Sample surface after immersed in saltwater for 3 months



Fig. S12 SEM images displaying the surface morphology of samples after immersion in 3.5 wt% NaCl solution at 25 °C for 3 months. (a) 5N AI, (b) Al3Mg, (c) Al0.1In. The areas in marked in red circles indicate the pits

When samples were immersed in 3.5 wt% NaCl solution at 25 °C for 3 months, pure Al (Fig. S12a) and Al0.1In (Fig. S12c) exhibit pitting, while Al3Mg (Fig. S12b) and Al3Mg0.1In (Fig. 4a) pitting effects are less.

S13. Sample surface morphology before and after discharge



S13.1 Sample surface morphology before discharge

Fig. S13.1 SEM images showing the surface morphology of bare samples before cell discharge: (a) 5N Al, (b) Al3Mg, (c) Al0.1In, (d) Al3Mg0.1In

S13.2 Sample surface morphology after discharge





Fig. S13.2 SEM images showing the surface morphology of samples after cell discharge with Pt/C cathode in 3.5 wt% NaCl solution at 25 °C for 24 hours. The sample composition and discharge current densities are listed below.

Sub Figure	1 mA/cm ²	15 mA/cm ²	30 mA/cm ²
5N AI	а	b	С
Al3Mg	d	е	f
Al0.1In	g	h	i
Al3Mg0.1In	j		k



S14. Surface roughness analysis of discharged samples using 3D Profilometer

Fig. S14 Optical surface profiles of samples after discharge at 15 mA/cm² in 3.5 wt% NaCl solution at 25 °C for 24 h. (a) 5N Al, (b) Al3Mg, (c) Al0.1In. Regions of deep pits are shaded in dark blue color.

S15. SEM elemental mapping of Al3Mg0.1In after discharge



Fig. S15 SEM elemental mapping of Al3Mg0.1In after discharge at 15 mA/cm² in 3.5 wt% NaCl solution at 25 °C for 24 h



S16. SEM elemental mapping of Al0.1In after discharge

Fig. S16 SEM elemental mapping of Al0.1In after discharge at 15 mA/cm² in 3.5 wt% NaCl solution at 25 °C for 24 h

S17. Mass calculations – examples

S17.1. SWB

Consider Al0.1In anode and Pt-C cathode with an initial gap of 5 mm, at 20 °C. At a current density of 1 mA/cm², the discharge potential is 1 V, and the corrosion rate is 0.049 mg/cm²/h, i.e., 0.18 μ /h. Since Al is the major constituent element in these alloys, the atomic weight and density of Al is used in all the calculations.

S17.1.1 Thickness calculations:

At a current density of 1 mA/cm², the corresponding metal dissolution rate is = $\frac{1 \times 10^{-3}}{3 \times 96485} \times \frac{26.98}{2.7}$ = 3.45×10⁻⁸ cm/s 1.24 µm/h.

Here, *i* is in A/cm², n is the number of electrons, *F* is the faraday constant, *AW* is atomic weight in g/mol, and r is the density in g/cm³.

Self-corrosion rate = 0.18 m/h

The total dissolution rate = 1.24 + 0.18 = 1.42 m/h.

Endurance requirement = 12 months = 12 × 30 × 24 = 8640 h

Thickness required = 1.42 × 8640 = 12,269 m = 12.269 mm ≈ 12.3 mm.

Anode efficiency = $\frac{1.24}{0.18 + 1.24}$ = 87.3%

S17.1.2 Electrode area calculations:

Power generated per unit area = V × i

Initial cell gap = 5 mm (same as the cell gap in the experiments conducted in the lab)

Initial cell potential = 1.00 V (measured in the lab).

At the end of operation, the cell gap would have increased by the thickness, i.e. 12.3 mm = 1.23 cm.

Sea water resistivity = 20.83 W-cm.

Corresponding iR drop, at the end of operation = 1.23×0.001× 20.83 = 0.026 V.

 \therefore final cell potential = 1-0.026 = 0.974 V

Power density (i.e., per unit anode area) at the end of operation= $0.974 \times 0.001 = 0.000974$ W/cm² = 0.974 mW/cm².

Sufficient power must be generated when the battery is nearing the end of life. At earlier times, more power will be available since the anode thickness will be more, and the iR drop will be less than that at the end of life.

Battery power requirement specification = 5 W

: anode area required = $5 / (0.974 \times 10^{-3}) = 5,133 \text{ cm}^2$.

S17.1.3 Mass calculations:

Volume of anode required = thickness × area = $1.23 \text{ cm} \times 5,133 \text{ cm}^2 = 6,314 \text{ cm}^3$

Mass of anode required = volume × density = 6,314× 2.7 = 17,048 g = 17.048 kg.

Cathode Mass per unit area = 5 g/100 cm² = 5×10^{-5} kg/cm²

Cathode mass = area × (mass/area) = $5133 \times 5 \times 10^{-5} \approx 0.257$ kg

Anode + cathode mass = 17.048 + 0.257 ≈ 17.3 kg

Example calculations for two other current densities are provided below for comparison.

	Current Density (mA/cm ²)			
	0.1	1	5	
Endurance requirement (months)	12	12	12	
Power requirement (W)	5	5	5	
Cell Voltage (V)	1.15	1	0.91	
Self corrosion rate (m/h)	0.094	0.18	0.68	
Anode density (g/cm ³)	2.7	2.7	2.7	
Cathode mass/area (kg/cm ²)	5.00E-05	5.00E-05	5.00E-05	

Metal dissolution rate due to	3.45221E-09	3.45221E-	1.73E-07
discharge (cm/s)		08	
Metal dissolution rate due to	0.12	1.24	6.21
discharge (m/h)			
Self corrosion rate (m/h)	0.094	0.18	0.68
Total dissolution rate (m/h)	0.21	1.42	6.89
Endurance requirement (h)	8640	8640	8640
Thickness required (mm)	1.8	12.3	59.5
Anode efficiency (%)	56.1%	87.3%	90.1%
Sea water resistivity (ohm-cm)	20.83	20.83	20.83
iR drop increase at the end of life	0	0.026	0.62
(V)			
Final cell potential (V)	1.15	0.974	0.29
Power density (mW/cm ²)	0.115	0.974	1.45
Anode Area required (cm ²)	43478	5133	3448
Anode volume required (cm ³)	7826	6314	20516
Mass of anode required (kg)	21.13	17.048	55.393
Cathode mass (kg)	2.174	0.257	0.172
Total anode + cathode mass (kg)	23.3	17.3	55.6

Assumptions:

A factor of 2 (i.e., 100% additional mass) of the sum of the components (anode + cathode), is used to account for parasitic losses, DC-DC conversion loss and reduction in the performance over a long time.

<u>Justification</u>: Two or three cells in series will be required to obtain a minimum potential of 2 V; since the cells are in open architecture, there will be a parasitic loss when the cells are in series, and the loss is assumed to be ~25%. DC-DC converter is usually required to boost the

cell voltage to usable voltage (e.g. 2 V to 24 or 48 V) and a DC-DC conversion efficiency of ~90% is assumed. For a given current density, compared to the cell voltage measured in 24 h period, the measured voltage over a longer-period shows ~20% reduction (Fig 5c and d). Likewise, the self-corrosion rate requires a 15 % buffer. Effectively, 75% × 90% × 80% × 85% ~46% power generated in individual cells is available at the voltage required by the user. Therefore 120% additional cells are required to meet the specifications.

- 2. Current collector and structural material mass depends on the cell dimensions and design, and is assumed to be 80% of the original (anode + cathode) mass.
- Essentially, the total pack mass is calculated as thrice the (anode+ cathode) mass estimated before accounting for parasitic and DC-DC conversion losses, and decrease in the voltage over time.

Calculations:

Anode + cathode mass accounting for parasitic and DC-DC conversion losses = $17.3 \times 2.2 \approx$ 38.1 kg.

Current collector and structural material mass = original (anode + cathode) mass = 13.8 kg

Total pack mass = 38.1 + 13.8 ≈ 52 kg

S17.2. Pressure tolerant lithium-ion battery pack

* Based on SWE website

https://www.swe.com/media/files/files/6062e688/2014 01 08 UI2014 Safe Configurable Pressure Tolerant Subsea Lithium Ion Battery System for Oil and Gas Deep Water Fi elds and ROVs - Leon Adams David Whitex.pdf, accessed on 17 Jul 2024.

Module Mass = 9.09 kg

Module Power = 1160 W

Module Energy = 812 Wh

The power requirement of 5 W is easily met by a single module. However, the energy requirements need = Total energy required/ module energy

= 43,200/812 = 53.2 = 54 modules. Self-discharge is assumed to be negligible.

Mass of Pressure tolerant LiB modules ≈ 491 kg

S17.3. Primary Li pack

*Based on lithium thionyl chloride cell values

https://robu.in/product/forte-er34615-d-3-6v-li-socl2-battery, accessed on 17 Jul 2024.

Single cell values.

Cell Potential = 3.6 V, Continuous current = 0.15 A, Capacity = 20 Ah, Mass = 108 g, cost = \$10. Self-discharge rate is assumed to be negligible.

Single Cell Power = $3.6 \times 0.15 = 0.54$ W

Single cell energy = 72 Wh

Number of cells required = 43200/72 = 600

Total pack mass = $600 \times 0.108 \approx 65$ kg

These cells must be kept inside the high-pressure chamber. Correspondingly, the total mass in the AUV will increase further. We assume that the increase in mass is 100%

Total pack mass, accounting for pressure chamber = 2 × 65 = 130 kg

S18. Cost estimates – example

Battery requirements are 5 W and 12 months, i.e. 43.2 kWh

S18.1 SWB

The cost values of the materials and fabrication will vary depending on the source and the scale. The following estimates have some uncertainty, and are provided as guidelines.

Assumptions:

- Anode alloy cost = \$30/kg
- Cathode cost = \$1.00 /cm²
- Factors accounting for structural materials, fabrication, DC-DC conversion electronics, business operations and profit = 200% of original (anode + cathode) cost.

Calculations:

Total anode cost = anode mass × anode cost per unit mass = 17.048 × 30 = \$511.

Total cathode cost = area × 1.00 = 5133× 1 = \$5,133

Total (anode + cathode) cost = \$5,644

Total SWB pack cost = 3 × 5644= \$16,932

Example calculations at two other current densities are shown below for comparison

	Current Density (mA/cm ²)			
	0.1	1	5	
Anode cost (\$/kg)	30	30	30	
Cathode cost (\$/cm ²)	1	1	1	
Anode mass (kg)	21.13	17.048	55.393	
Cathode area (cm ²)	43478	5133	3448	
Anode cost (\$)	634	511	1662	
Cathode cost (\$)	43478	5133	3448	
Anode + Cathode cost (\$)	44112	5644	5110	

Total pack cost (\$)	132336	16932	15330

S18.2 Pressure tolerant lithium-ion pack

Assumptions:

- Cost of an 18650 Li-ion cell of capacity 11.1 Wh (3.7 V, 3 Ah) ≈ \$8 https://www.electronicscomp.com/samsung-inr18650-30q-3000mah-5c-li-ionbattery, accessed on 17 Jul 2024.
- Cost of pressure tolerant LiB pack is assumed to be 100% higher than that of a normal LiB pack.

Calculations:

Normal 18650 Li-ion cell cost per energy =\$8/11.1 = \$720/kWh.

Normal LiB pack cost = cost/unit energy × energy required = 720 ×43.2 = \$31,104

Pressure tolerant LiB pack cost =31,104 × 2 = \$62,208

S18.3 Primary Li pack

Assumptions:

- Single cell values. Cell Potential = 3.6 V, Continuous current = 0.15 A, Capacity = 20 Ah, Mass = 108 g, cost ≈ \$10
- Cost of incorporating the primary cells in pressure chamber = 100% of the pack cost

Calculations:

Number of cells required = 43200/72 = 600

Total pack cost = \$6000

Total pack cost inside the pressure chamber = $2 \times 6,000 = $12,000$

S19. Mass and Cost vs. Current Density

S19.1 5W, 12 months

Battery pack specifications are 5 W power and 12 months endurance. Please note that high purity Al cost is taken as \$800/kg and hence the pack costs are very high compared to those of other alloys. For all other alloys, anode cost is taken as \$30/kg.



Fig. S19.1 Battery pack mass and cost estimates as a function of current density, for several anode materials, for 5 W power and 12 months endurance requirements.

S19.2 33 W, 4 months

Battery pack specifications are 33 W power and 4 months endurance. Pack mass and cost at several operating current densities are shown below.





Fig. S19.2 Battery pack mass and cost estimates as a function of current density, for several anode materials, for 33 W power and 4 months endurance requirements.

S20. A photograph of the electrode surface after long duration discharge



Fig. S20 photograph of the electrode surface of Al3Mg0.1In after discharge at 2.8 mA/cm², in 3.5 wt% NaCl solution at 20 °C after 1 month

S21. Experiments with larger area cells

<u>Experimental:</u> A "90 cm² area cell" was created using an anode of 10 cm × 10 cm × 0.5 cm, and with a cathode of 10 cm × 10 cm × 0.05 cm thickness. Four holes were cut in the cell to facilitate passing nylon screws. The cell was assembled using nylon screws, washers and nuts (Fig. S20.1 a and b). The edges of the anodes were covered with epoxy. The side of the anode not facing the cathode was also covered with epoxy. The side of the cathode not facing the anode was protected by a Teflon[®] sheet of 10 cm × 10 cm × 1 cm. Thus, only the anode and cathode areas exposed to each other were involved in cell reactions. The total initial cell mass was 171 g, out of which cathode mass was 2 g, anode mass was 133 g and the mass of epoxy, Teflon sheet and nylon screws was 36 g. The ratio of the mass of inactive materials to the total mass is 21%.

A "450 cm² area cell" was created using one anode of 10 cm × 10 cm × 0.5 cm size, two anodes of 10 cm × 10 cm × 1 cm size, and five cathodes of 10 cm × 10 cm × 0.05 cm size (Fig. S20.1 c and d). The total initial cell mass was 727 g, out of which cathode mass was 10 g, anode mass was 644 g and the mass of epoxy, Teflon sheet and nylon screws was 73 g. The anode density was slightly lower in this cell; it is possible that some air was trapped in the anode during the casting process. The ratio of the mass of inactive materials to the total mass is 10%.

The experiments were conducted at room temperature (between 26 and 27 °C) at 0.4 mA/cm² corresponding to minimum mass of 5-W, 12-month requirement, for 7 days.







Fig. S21.1 (a) A photo of a 90 cm² area cell (b) a schematic showing the connections and anode thickness values of 90 cm² area cell (not drawn to scale). (c) A photo of a 450 cm² area cell. (d) A schematic showing the connections and anode thickness values of 450 cm² area cell (not drawn to scale). All the electrodes were square shaped with 10 cm width and 10 cm length.

<u>Results</u>: The results of the "90 cm² area cells" are shown in Fig.S20.2a. The cell potential fluctuated mostly between 0.86 and 1.2 V, and the average value was 0.925 V. The trends are quite repeatable. The power produced is 33.3 mW. The results of "450 cm² area cell" are shown in Fig. S20.2b. Here again, the cell potential fluctuated between 0.88 and 1.2 V, and the average value was 0.936 V. In comparison, the cell potential obtained using 1 cm² area electrodes at 25 °C was 1.1 V. Thus, scaling up to 90 and 450 cm² area results in a loss of ~15% in cell potential. On the other hand, at 0.4 mA/cm² current density, the self-corrosion rate was found to be 0.03 μ m/h (0.0226 ± 0.011 μ m/h, which is approximated as 0.03 μ m/h) for the 90 cm² area cells, and 0.0331 μ m/h for the 450 cm² results in a decrease in corrosion rate by 56 ± 2 %. It is possible that the corrosion and dissolution product build up near the surface has retarded the self-corrosion rate and reduced the cell potential.

Fig. S21.2 Cell potential as a function of time for (a) 90 cm² cells (b) 450 cm² cells. The anode was Al3Mg0.1In and cathode was Pt/C. The electrolyte was 3 wt% NaCl at room temperature. The operating current density was 0.4 mA/cm²

The results of 90 cm² area cells show that the anode, with an initial mass of 133 g and 5 mm thickness, would last for 396 days while producing 33 mW at 0.925 V. The corresponding values of 450 cm² cells are 393 days and 168 mW at 0.936 V. Therefore, the endurance requirement is met with some buffer, and a slightly thinner electrode would be sufficient to satisfy the specification. Since the corrosion rate and potential values of 90 and 450 cm² cells are within experimental error, the results of 90 cm² cells are used for further calculations.

A direct extrapolation of the 90 cm² area cell results indicates that the mass of a cell producing 5 W at 0.925 V for 12 months would be 26 kg. Of this, 20% would be inactive material. When a DC-DC converter efficiency of 70% is accounted for, the pack mass would be 37.1 kg.

Our calculations based on the 1 cm² area results shown in the manuscript indicate that, for operation at 25 °C, with 5-W 12-month endurance requirement, the pack mass would be 43.9 kg. This leaves a buffer of 6.8 kg (~ 15% of 43.9 kg). It is to be noted that these estimates are extrapolations. Experiments with large pack producing the target power should be run for the actual endurance requirement to validate and refine the model calculations.

S22. Power-Endurance contour plots

The contour plots of SWB shown below correspond to the minimum pack mass. Usually, the operating current density for minimum pack mass and minimum pack cost are different. i.e., the SWB pack cost can be significantly lower than the values shown in the contour plots, if a higher pack mass is acceptable.

S22.1 Short duration (1-48 h)

Please note that in the case of SWB, the total cost is dominated by the cathode cost, and slight changes in the cathode requirements lead to large change in the cost. Hence, the cost contour plots of SWB are not smooth. In the case of 5N Al, the anode cost is also very high.

(a) 5N AI

Fig. S22.1.1 Power endurance contour plot of 5N Al for short duration (1-48 h) application

(b) Al3Mg

Fig. S22.1.2 Power endurance contour plot of Al3Mg for short duration (1-48 h) application

Fig. S22.1.3 Power endurance contour plot of Al0.1In for short duration (1-48 h) application

(d) Al3Mg0.1In

Fig. S22.1.4 Power endurance contour plot of Al3Mg0.1In for short duration (1-48 h) application

Amongst the SWB, the ones with Al0.1In anode have the lowest mass for the short duration requirements. The optimal operating current density depends mainly on the duration and not on the power required.

(e) Pressure Equalized LIB

Fig. S22.1.5 Power endurance contour plot of LIB for short duration (1-48 h) application

PT Li secondary cells chosen here are available in \sim 10 kg pack and hence the choices are limited to multiples of 10 kg.

(f) Primary Li battery

Fig. S22.1.6 Power endurance contour plot of Primary Li battery for short duration (1-48 h) application

In short duration, Li-primary pack can easily meet the energy requirement, but the power requirements need several cells to make the pack. Therefore, the mass and cost are independent of duration in this range.

Overall, for short duration requirements, LiB pack is the best choice, especially since it is reusable.

S22.2 Medium duration (1-30 days)

(g) 5N Al

Fig. S22.2.1 Power endurance contour plot of 5N Al for medium duration (1-30 days) application

Fig. S22.2.2 Power endurance contour plot of Al3Mg for medium duration (1-30 days) application

(i) Al0.1In

(h) Al3Mg

Fig. S22.2.3 Power endurance contour plot of Al0.1In for medium duration (1-30 days) application

Fig. S22.2.4 Power endurance contour plot of Al3Mg0.1In for medium duration (1-30 days) application

(k) Pressure Equalized LIB

Fig. S22.2.5 Power endurance contour plot of LIB for medium duration (1-30 days) application

(I) Primary Li battery

Fig. S22.2.6 Power endurance contour plot of primary Li battery for medium duration (1-30 days) application

For medium duration requirements, Li-primary appears to be the best choice. Although LiB packs are rechargeable, the pack mass is very high. SWB have a slightly lower mass than Li-primary packs, but the cost is significantly higher.

Fig. S22.3.1 Power endurance contour plot of 5N Al for long duration (30-365 days) application

(n) Al3Mg

Fig. S22.3.2 Power endurance contour plot of Al3Mg for long duration (30-365 days) application

Fig. S22.3.3 Power endurance contour plot of Al0.1In for long duration (30-365 days) application

(p) Al3Mg0.1In

Fig. S22.3.4 Power endurance contour plot of Al3Mg0.1In for long duration (30-365 days) application

(q) Pressure Equalized LIB

Fig. S22.3.5 Power endurance contour plot of LIB for long duration (30-365 days) application

(r) Primary Li battery

Fig. S22.3.6 Power endurance contour plot of primary Li battery for long duration (30-365 days) application

For long duration requirements, SWB is the best choice. The pack mass is less than half of the Li-primary pack mass and nearly one tenth of LiB pack mass. The cost is more than that Li-primary pack cost and less than LiB pack cost. However, the operating current density can be changed to significantly reduce the pack cost while increasing the pack mass only slightly, as shown in Fig. 7b of the manuscript. Thus, both the cost and mass of SWB would be less than the respective cost and mass of Li based packs.

2. References

1. R. Srinivasan and F. Fasmin, *An introduction to electrochemical impedance spectroscopy*, CRC Press, 2021.