Safety Assessment of Scenarios Triggered by Accidental Seawater Immersion of Lithium Batteries in Innovative Naval Applications

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The request of lithium-ion batteries in naval applications features an increasing trend due to the need of high performance energy storage devices. Beside the hazard of runaway when the battery is crushed or overcharged, the naval environment poses additional safety issues due to the possible immersion with seawater of the battery room following accidental flooding. In such a case, seawater electrolysis may generate hydrogen and chlorine, thus giving rise to an explosive and toxic mixture in a confined environment. In this study, a quantitative safety assessment of the possible accidental scenarios induced by seawater electrolysis in battery rooms is performed. The analysis is based on i) the deterministic evaluation of the hazardous gases development according to a three-dimensional physically-based electrochemical model and ii) the discussion of possible prevention and mitigation measures. The dynamics of gas release and the time required to produce an explosive atmosphere are evaluated as a function of the level of seawater for a reference case study. The outcomes of the study support the safety assessment of accidental scenarios induced by seawater electrolysis in naval applications and provide indications on the effectiveness of hazard reduction measures. More specifically, the study reveals that a proper electric insulation of the surface of battery terminals represents a sensible mitigation strategy to reduce the severity of explosions in addition to the ventilation of the battery room.

1. Introduction

After the launch of the first electric ferry in Norway in 2015, there has been an increasing interest in ships and yachts powered by large batteries (Mashayekh et al., 2012). The use of lithium-ion batteries in naval applications as energy storage devices and auxiliary power units has several benefits, such as the possibility to moor and/or access in noise-free or pollution-free harbours. However, some safety issues arise when such large battery systems are used in enclosed environments such as a pleasure boat. In addition to the hazard of runaway reactions (Finegan et al., 2015) as a consequence of battery overcharge or accidental puncture of the battery case, the naval environment poses additional threats which are not normally taken into account in standard safety tests for onshore applications (Demeestere et al. 2016). In particular, in case of accidental flooding of the battery room, seawater may come in contact with the battery terminals, thus creating an external short circuit and producing H_2, O_2 or Cl_2 through the following electrolysis reactions:

$$2H^+ + 2e^- \rightarrow H_2 \tag{1}$$

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^- \tag{2}$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{3}$$

where hydrogen evolution (Eq. (1)) takes place at the negative terminal while oxygen/chlorine evolutions (Eqs. (2-3)) are competing reactions at the positive terminal. Therefore, the potential formation of an explosive and toxic enclosed atmosphere must be carefully taken into account.

This study proposes a methodology, based on electrochemical modelling (Bertei et al., 2013), to quantify the dynamic evolution of gases in a reference battery room installation as a function of the severity of the flooding scenario. The time required to form an explosive atmosphere is quantified and compared with the minimum intervention time. Finally, strategies specifically tailored to mitigate the severity of explosion scenarios in naval applications are summarised.

2. Methodology

2.1 Description of the reference case study

The battery room considered in this study contains 780 battery modules (Figure 1), each one having a nominal capacity of 82 Ah and a nominal open circuit potential of 53.2 V when fully charged. In case of accidental flooding of the battery room, seawater electrolysis (Eqs. (1-3)) can take place between the positive and negative terminals of each battery module (Figure 2a and 2b), being the potential difference between the terminals larger than the equilibrium potential of seawater electrolysis, thus creating an external short-circuit and discharging the module completely (Figure 2c). During discharge, the potential difference between the terminals of each module can be considered fairly constant and equal to 45.5 V as from experimental testing (Saft, 2018). By considering this potential difference between the terminals, the internal resistance of the module is implicitly taken into account.
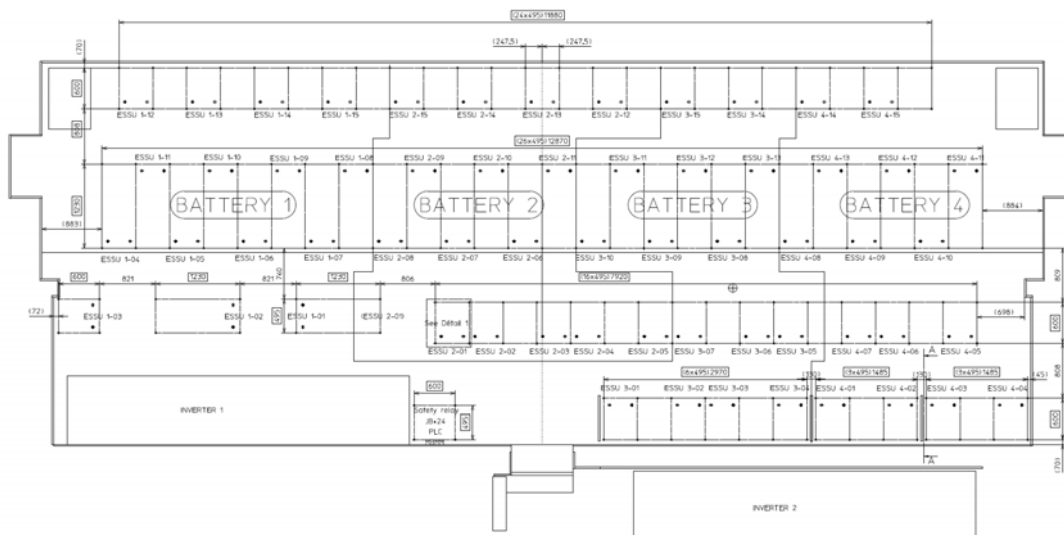

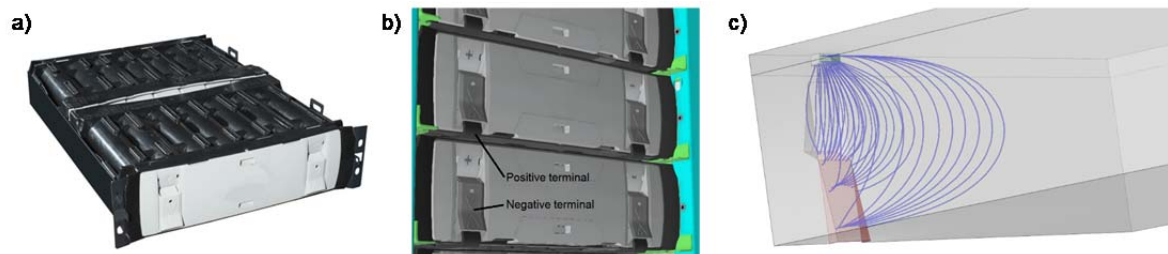Figure 1: Layout of the battery room. The ceiling is placed at 2081 mm from the floor. Distances are in mm.

Figure 2: a) View of a standalone battery module. b) View of battery modules in a rack. c) Simulated current distribution (blue streamlines) due to seawater electrolysis between the exposed surface of negative (red) and positive (green) terminals of a battery module.

2.2 Model

The electrochemical simulation aims to assess the current circulating within seawater between the two terminals as a consequence of seawater electrolysis. In the worst-case scenario, the terminals are unprotected by any external coating. The calculation of the current allows for the determination of the hydrogen flowrate produced at the negative terminal and the time required to completely discharge the module. The reference temperature of 25 °C is considered.

The simulation domain to assess the electrolysis current distribution consists of the volume of seawater in front of each battery module. Such a simulation domain is as high as the module height (147 mm), as wide as the module lateral width (448 mm) and as deep as the semi-distance between two racks (404 mm, see Figure 1). The model, summarised in Table 1, takes into account the following phenomena:

- primary current distribution within seawater (Table 1, Eq. (4)), taking into account the seawater ohmic conductivity σ (4.3 S/m, Culkin and Smith, 1980). The potential is set equal to 45.5 V at the positive terminal and E° = 1.23 V at the negative terminal (i.e., the equilibrium potential of seawater electrolysis). By integrating the current density entering the negative terminal, the current I can be calculated.
- activation overpotential of hydrogen evolution reaction at the negative terminal (Table 1, Eq. (5), Zeng and Zhang, 2010). This contribution takes into account the additional resistance due to the kinetics of hydrogen evolution.
- dynamic transport of hydrogen in seawater. The transport of dissolved hydrogen takes place according to diffusion as in Eq. (6) (diffusivity $D = 4.91 \cdot 10^{-9}$ m^2/s, Jähne et al., 1987) when the hydrogen concentration C is lower than the solubility limit (0.786 mol/m^3). Beyond the solubility limit, hydrogen bubbles evolve and rise upwards according to the terminal velocity u (Table 1, Eq. (7), Talaia, 2007), where ρ_l is the density of seawater (~1000 kg/m^3), ρ_g the density of the hydrogen bubble (0.0818 kg/m^3), μ_l the viscosity of seawater (10^{-3} kg/(m·s)), g the gravity constant (9.81 m/s^2) and d the bubble diameter (assumed 2 mm).

The molar flowrate of hydrogen J (mol/h) produced by each module upon electrolysis is determined as in Eq. (8), where F is the Faraday constant (96,485 C/mol) and I (in A) is the electrolysis current produced by the module. The total molar flowrate is equal to the product of J and the number of modules completely immersed in the specific flooding scenario. The current I is also used in Eq. (9) to evaluate the time T (h) required for a complete discharge of the module upon seawater electrolysis, where Q is the nominal capacity of the battery module (82 Ah). Comsol Multiphysics® 5.2 is used to solve the model equations.

Table 1: List of model equations.

Phenomenon	Model equation	Eq.
Primary current distribution	$\nabla \cdot (-\sigma \nabla V) = 0$	(4)
Kinetics hydrogen evolution	$i = 4 \cdot 10^{-2} \cdot \exp\left((V - E°) / 0.120\right)$ A/m^2	(5)
Transport dissolved hydrogen	$\partial_t C + \nabla \cdot (-D \nabla C) = 0$	(6)
Bubble rise velocity	$u = \left(\rho_l - \rho_g\right) g d^2 / \left(18 \mu_l\right)$	(7)
Hydrogen flowrate	$J = 3600 \cdot I / \left(2F\right)$	(8)
Time for complete discharge	$T = Q / I$	(9)

3. Results

3.1 Results for the unprotected scenario

In the unprotected scenario the whole external surface of the positive and negative terminals is considered active for seawater electrolysis. Figure 2c shows that the simulated current streamlines (in blue) originate from the positive terminal (green, at the top) and spread only within the seawater volume in the proximity of the terminals for about 100 mm, without extending throughout the whole volume in front of the module. The current preferentially flows within the shortest distance between the terminals, showing a higher current density in the upper sloping region of the negative terminal. Such a confined current distribution suggests that any mitigation strategy aimed to reduce the electrolysis current must be implemented in the proximity of the terminals. On the contrary, decreasing the distance between the racks in order to impede current flow would be ineffective because the racks should be placed too close each other (i.e., in the order of 100 mm) in order to perturb the current distribution.

By taking into account both the primary current distribution (Eq. (4)) and the kinetic resistance of hydrogen evolution (Eq. (5)), the predicted electrolysis current is equal to I = 6.32 A, which is equivalent to a molar

hydrogen flowrate J of 0.12 mol/h and a discharge time of 12 h 58 min per module. Notably, the model predicts a current density of 17,250 A/m^2 at the positive terminal. This value exceeds the limiting current density of 10,000 A/m^2 for Cl_2 evolution (Abdel-Aal et al., 2010). This means that, according to model predictions, Cl_2 evolution should be impeded at the positive terminal, thus O_2 evolution is favoured instead of Cl_2 evolution. This prevents the formation of a toxic environment upon seawater electrolysis.

By taking into account the hydrogen dissolution and diffusion in seawater (Eq. (6)), it is possible to assess if the hydrogen produced by electrolysis remains dissolved in seawater and how long it takes to travel upwards from the negative terminal to the water interface, thus being released in the battery room atmosphere with a time delay. Simulations indicate that diffusion is too slow to carry hydrogen away from the negative terminal surface, being the simulated local concentration larger than the solubility limit. Therefore, rather than remaining dissolved in seawater, hydrogen will be likely released as gas bubbles, which will rise upwards quite rapidly with an estimated velocity of 2.2 m/s (see Eq. (7)). Such a high bubble velocity means that hydrogen is almost instantaneously released in the battery room atmosphere as soon as it is electrochemically produced at the negative terminal. The fraction of hydrogen which remains dissolved in seawater is negligible due to its low solubility limit and low diffusivity.

3.2 Results for the mitigated scenario

A possible mitigation strategy consists in protecting the external surface of the terminals with an electric insulator (Figure 3a). In such a case, a large fraction of the terminal surface is not exposed to seawater, so electrolysis and hydrogen evolution cannot not take place in those areas. It is assumed that, due to possible inaccuracies, 2 mm of the terminal surface may remain unprotected, as depicted in Figure 3b. In such a case, electrolysis and hydrogen evolution take place only at the narrow red and green stripes in Figure 3b.

By taking into account both primary current distribution in seawater (Eq. (4)) and the kinetic resistance of the hydrogen evolution reaction at the negative terminal (Eq. (5)), the predicted current distribution for the protected scenario is shown in Figure 3c. Figure 3c shows that the current streamlines (in blue) originate from the narrow unprotected stripe at the top of the positive terminal (green) and reach the narrow unprotected stripe at the bottom of the negative terminal (red) while spreading in seawater only within the first 100 mm.

The reduced exposed surface area of the terminals causes a substantial decrease in the electrolysis current, which is reduced to I = 1.75 A, that is, 3.6 times smaller than the unprotected scenario discussed in the previous section. Accordingly, the time required to completely discharge the immersed battery modules rises to T = 46 h 45 min and the hydrogen flowrate falls to J = 0.033 mol/h per module. In practice, by protecting the terminal surfaces with an insulation, the discharge current and hydrogen flowrates can be decreased by a factor 3.6 with a corresponding increase in the discharge time.

Similar to the unprotected case, a very slow diffusive transport is predicted according to Eq. (6) so that the dissolved hydrogen concentration exceeds the solubility limit. Therefore, also in the protected scenario, hydrogen is released in form of bubbles, which rise almost instantaneously up to the seawater interface and release hydrogen directly in the battery room atmosphere. Thus, even in this mitigated scenario the fraction of hydrogen which may remain dissolved in seawater is negligible. In addition, model simulations predict an average current density as high as 36,500 A/m^2 at the exposed surface of the positive terminal, which should favour O_2 evolution rather than Cl_2 evolution, thus preventing toxic release also in this case.
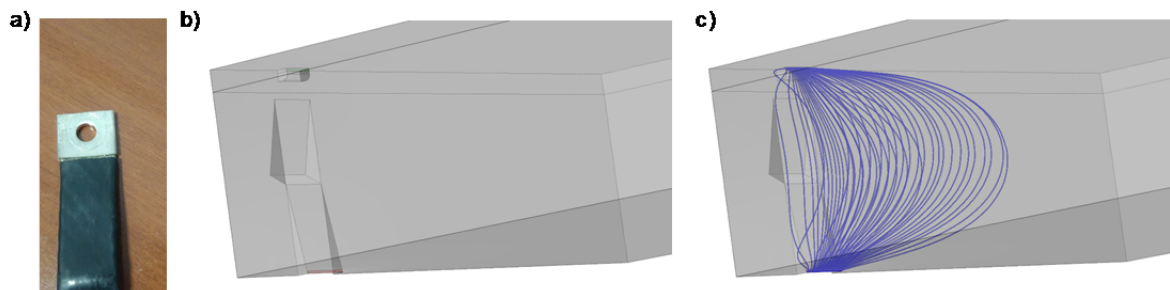

Figure 3: a) Insulation of the positive terminal. b) Schematic view of the exposed terminal surfaces in case of insulation: only two stripes 2 mm wide are left. c) Simulated current distribution in the mitigated scenario.

4. Discussion: hazard reduction strategies

The development of hydrogen in a confined space such as the battery room may create a flammable atmosphere, giving rise to a potential explosion in case of ignition. Accident investigations (Bjerketvedt et al., 1997) show that some injurious or fatal explosions are caused by a quantity of fuel gas significantly less than that required to fill the entire enclosure volume to the stoichiometric condition. There are consolidated methods in the literature (Jo and Park, 2004) for calculating the minimum gas quantity required to cause a specified damage level of explosion to prepare countermeasures in the phase of hazard analysis. A typically adopted approach is based on the calculation of the quantity of fuel gas that corresponds to filling the enclosure volume to the lower flammable limit (LFL) concentration with homogeneous distribution. In this specific case, the quantity of fuel gas in the enclosure depends on the number of immersed battery modules for any specific flooding scenario.

Due to relevant uncertainties in the analysis of the flooding scenario, a parametric study is performed on the flooding height, varying it from 0 to the total height of the battery room (2081 mm). The time required to reach an explosive atmosphere as a function of the flooding height can be estimated from the hydrogen flowrate per unit of immersed battery module, J, as discussed in the previous sections. Such a calculation takes into account the layout and volume of the battery room, the arrangement and volume of the battery units (Figure 1) and thus the number of modules immersed in seawater for any given level of water. Thus, the total hydrogen flowrate is evaluated and assumed to be homogeneously released in the closed atmosphere above the water level, assuming no ventilation in the battery room.

However, the concentration distribution of gas in the enclosure is affected by the density of gas, release velocity and height of the source, whose effects are out of the scope of the present study. Therefore, in order to overcome this limitation in the model, the recommendations reported by Jo and Park (2004), who indicate an explosion hazard even for concentrations lower than LFL, are considered. A safety margin is introduced in the analysis, thus the safety limit to avoid explosion is considered as between 10 % and 50 % of the LFL concentration. Therefore, a parametric analysis as a function of the flooding height is performed for concentration limits equal to 10 % and 50 % of the hydrogen LFL (where LFL = 4 % v/v). Results are reported in Figure 4.
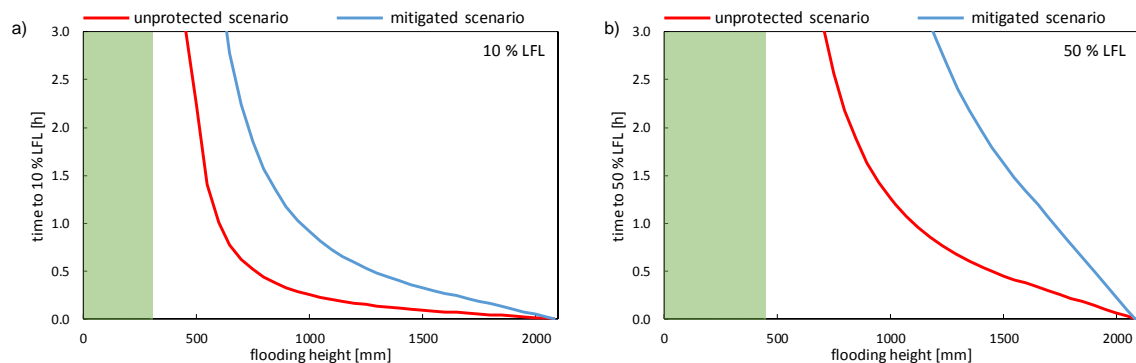

Figure 4: Calculated time required to reach an explosive atmosphere as a function of the water level in the battery room for the two scenarios for a) 10 % LFL and b) 50 % LFL.

Figure 4 shows that the time required to reach the concentration limit decreases as the level of seawater increases. For a flooding height smaller than 241 mm, no hydrogen is released as no module is immersed. As the water level rises, more battery modules are immersed, releasing more hydrogen through electrolysis within a closed atmospheric volume, whose size decreases as the water level increases. Notably, for low water levels, just a few battery modules are immersed, so that the total hydrogen released within the predicted discharge time (12 h 58 min and 46 h 45 min for unprotected and mitigated scenarios, respectively) is not sufficient to reach the concentration limits. This situation is represented by the shaded green areas in Figure 4. Beyond this point, as the water level increases, more battery modules are immersed and less empty volume is left above the water level, therefore the time necessary to reach the concentration limit decreases. For a given flooding height, a shorter time to reach the concentration limit is required in the unprotected scenario (red) than in the mitigated scenario (blue) due to the larger hydrogen flowrate per immersed module (0.12 mol/h vs 0.033 mol/h, respectively).

In absence of ventilation of the battery room, emergency procedures on board are critical to avoid the escalation of effects induced by possible confined fires and explosions. Inerting the battery room to reduce the oxygen molar fraction with an inert fluid (such as Novec 1230 – perfluoro(2-methyl-3-pentanone)) represents a sufficient safety barrier. The inerting system can be activated after the triggering of an alarm through a floating sensor, placed at a critical height in the battery room. According to Figure 4b, such a floating sensor can be precautionary placed at a height of 450 mm, which is the minimum flooding height corresponding to the formation of a flammable hydrogen-air mixture at 50 % LFL. While this height of 450 mm may seem too precautionary since several hours are required to reach explosive conditions, it should be noted that the water level is expected to rise with time in case of severe flooding.

All these considerations are valid under the assumption of no ventilation of the battery room. In case of ventilation, the formation of an explosive environment can be delayed or even prevented. Therefore, ventilation of the battery room is key in reducing the explosion hazard and should be considered in the design as a critical safety barrier in addition to inerting of the room.

5. Conclusions

The present study investigated the flammable gas release from the accidental contact between seawater and lithium batteries in naval applications. A reference case study was analysed evaluating the flammable gas release as a consequence of seawater electrolysis through electrochemical modelling. The flowrate of hydrogen released from each battery module was quantitatively assessed in both an unprotected scenario and in a mitigated scenario, in which battery terminals are protected with insulation. These results indicate that adopting an efficient external insulation of the terminals over time is essential to reduce the severity of accidental flooding scenarios.

The study also supported the development of emergency procedures assuming no ventilation in the battery room by determining the available time for operations on the basis of flooding scenario severity and proposing mitigation strategies, such as inerting the battery room activated by an alarm triggered by a floating sensor.

The present method was proved to provide an effective support for the quantitative safety assessment of flammable release in electric boats due to seawater electrolysis upon the flooding of the battery room and may be extended to other naval applications.

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