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Performance and Perspectives of an Acid/Base Flow Battery

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Recently, the utilisation of renewable energy sources is a matter of increasing importance in Europe for Energy Transition and to achieve energy independence. To this aim, tailored Electric Energy Storage (EES) devices must be employed to tackle the issue of fluctuating production from renewables. The Acid/Base Flow Battery (AB-FB) is a cutting-edge technology that allows energy to be stored in the form of acidic and alkaline solutions (van Egmond et al., 2018). This method employs two membrane processes, one for the charge phase and one for the discharge phase, namely Electrodialysis with Bipolar Membrane (EDBM) and Reverse Electrodialysis with Bipolar Membrane (REDBM), respectively. The polymeric membranes and the two electrodes are the main components of this battery. The AB-FB is a novel technology, and a lot of effort is needed to properly assess its current and future potential and identify the geometrical and operating conditions maximising its performance. This study presents a techno-economic analysis (TEA) carried out by using technically optimal results from a previous bi-objective optimisation (Culcasi, et al., 2022b). By assessing the sensitivity on the input parameters, the Levelized Cost of Storage (LCOS) of a battery operating in closed-loop and using current commercial membranes spanned from 0.17 € kWh−1 to 0.45 € kWh−1, indicating that the AB-FB has significant potential in the commercial market.

* 1. Introduction

Decarbonisation strategies in the energy sector are crucial in addressing climate change. Renewable energy sources are essential, but a significant mismatch between power generation and consumption must be tackled using energy storage systems (Baldinelli et al., 2020). Acid-Base Flow Batteries (AB-FBs) are a viable solution because they are safe and environmentally sustainable and work well with modern smart grids. The working principle of AB-FBs is based on the water dissociation reaction, which occurs in the bipolar membranes of the battery (van Egmond et al., 2018). During the charge phase, the electricity input is converted into acidic and alkaline solutions, and the neutralisation of the acidic and alkaline solutions during the discharge phase produces electricity again (Culcasi et al., 2021) (Figure 1). The AB-FB is made up of repeating units called “triplets” that consist of one anion- and one cation-exchange membrane and one bipolar membrane, which are separated by net spacers. Water dissociation proceeds in the BPM interlayer when an electric potential is applied, producing proton and hydroxide ions (Pärnamäe et al., 2021). There have been numerous studies on EDBM (Herrero-Gonzalez et al., 2020), which is used as the charge phase of the AB-FB, but few on the REDBM (discharge phase) (Zaffora et al., 2020). The studies have primarily focused on experimental analyses under various operating conditions and stack sizes.



Figure 1: Schematic representation of the Acid/Base Flow battery charge a) and discharge b) phases (Culcasi, et al., 2022b).

The AB-FB was first proposed by Emrén and Holmström (1983), who suggested storing energy in the form of acidic and alkaline solutions in BPM fuel cells. Later, Pretz and Staude (1998) evaluated the performance of an AB-FB with varying triplet numbers and solution concentrations, achieving 22% process efficiency. Zholkovskij et al. (1998) investigated the power density and specific energy of a single-triplet AB-FB at low acid/base concentrations. Furthermore, Kim et al. (2016) recently investigated a broader range of acid/base concentrations and achieved a maximum power density of 2.9 W m−2. They also related deviations in Open Circuit Voltage to detrimental phenomena. Studies on AB-FB stacks have demonstrated the presence of detrimental phenomena such as low water back-diffusion through BPM layers and high electrode overvoltages. Van Egmond et al. (2018) tested an AB-FB with one triplet and, at the maximum concentration, achieved an open circuit voltage of 0.83 V and a gross power density of 3.7 W m−2. Xia et al. (2020) examined an AB-FB with 5 to 20 triplets and reported a maximum power density of 15 W m−2 in the discharge phase; in their study, the performance of the unit was found to be affected by parasitic currents via manifolds. In Zaffora et al. (2020), a power density of 17 W m−2 was recorded with a stack of 10 triplets operated in once-through, while an energy density of ~10 kWh m−3 was estimated for a complete discharge. However, the experiments confirmed the presence of parasitic currents via manifolds, which increased with the number of triplets and the acid/base concentration. To diminish the level and the effects of parasitic currents, the stack can be designed with a reduced cross-sectional area of the manifolds; however, this may also cause significant pressure losses and poor distribution of the electrolyte solutions. An alternative design of the system consists of a multi-block.

Our previous research (Culcasi et al., 2022b) demonstrated that various operating and design features can significantly influence the performance during the charging and discharging phases of the energy storage systems. To optimise the net Round Trip Efficiency (RTEnet) and average discharge Net Power Density () simultaneously, we employed a bi-objective optimisation approach using the ε-constraint method. Utilising commercially available membranes and specific operating conditions and design features, we were able to maximise the RTEnet up to 64%, along with an of 4 W m−2. Conversely, could be maximised at 19.5 W m−2 under alternative operating conditions, resulting in an RTEnet of 32%. The optimisation study produced Pareto curves, representing the set of optimal solutions in the bi-objective optimisation problem. These curves reveal that any improvement in RTEnet requires a trade-off in , and vice versa. The Pareto curves are characterised by monotonic decrease and concave downward features, with RTEnet on the y-axis and on the x-axis. At lower current densities, voltage efficiency increases as external voltage approaches the open circuit condition during both the charging and discharging phases. In contrast, a higher discharge current density corresponds to elevated values, potentially indicating proximity to the power-current graph's peak.

Furthermore, it is crucial to consider additional parameters, such as Net Energy Density (NED), which holds considerable implications, particularly in relation to the volume footprint. A larger footprint can lead to increased system costs and spatial constraints, emphasising the need for optimisation in this area as well. Economic considerations are also essential in identifying cost-effective solutions for large-scale applications and reducing the Levelized Cost of Storage (LCOS). Pärnamäe et al. (2020) revealed that AB-FB has power subsystem costs of approximately 1,520 € kW−1, which is comparable to large-scale vanadium redox flow batteries at 1,000 € kW−1. However, the energy subsystem costs for ABFB are five to eight times lower. In another study (Díaz-Ramírez et al., 2022), a comparison between Vanadium Redox Flow Batteries (VR-FB) and AB-FB showed that VR-FBs have higher investment costs, estimated at 339 € kWh−1, which was nearly double the cost of the AB-FB system at 184 € kWh−1. Moreover, van Egmond (2018) demonstrated that the LCOS for AB-FB can vary significantly based on the application scope. For instance, an AB-FB used in an energy arbitrage scenario significantly outperforms a Transmission and Distribution (T&D) support scenario, with an LCOS of 0.26 € kWh−1 compared to 0.44 € kWh−1. In the present work, we delve into the net discharge energy density and conduct a techno-economic analysis (TEA) to identify the process conditions that impact the LCOS.

* 1. Method

In a previous work, we developed a multi-scale mathematical model for the AB-FB (Culcasi et al., 2020), which was then adapted by incorporating ad hoc equations to accurately predict the behaviour of the bipolar membrane during the charging (Culcasi, et al., 2022a) and discharging phases. The model was implemented in the gPROMS Model Builder® environment. The developed semi-empirical simulation tool describes the AB-FB process with phenomenological equations (for ions and water transport across membranes) containing membrane parameters, including electrical resistances and ion diffusivities, set by using experimentally predetermined values. The model outcomes showed that electro-membrane processes could be accurately simulated while maintaining an appropriate computational burden by integrating calculations of non-ideal phenomena, such as concentration polarisation, parasitic currents and pressure losses. Therefore, a bi-objective optimisation study was performed to explore the technical potential of the AB-FB in terms of average net discharge power density and net Round-Trip Efficiency (Culcasi et al., 2022b)

In this study, we extend our previous research by (i) presenting and discussing the net energy density in the discharge phase, as determined along the RTEnet- Pareto frontier using eight decision variables from our prior optimisation study (Culcasi et al., 2022), and (ii) conducting a techno-economic analysis (TEA) of the AB-FB system. The TEA evaluates the Levelized Cost Of Storage (LCOS) values along the same Pareto curve, and a sensitivity analysis is performed to examine the LCOS dependence on the model primary parameters at the two extreme optimal points (single-objective optimisations). The key aspects of the applied methodology are outlined below.

The electrolytes simulated for salt, acid and base were NaCl, HCl and NaOH, respectively. In the simulated AB-FB system, the solutions in the external reservoirs were assumed to have perfect mixing. Each simulation had a single round-trip cycle encompassing a charge phase followed by a discharge phase. For each round-trip cycle, the initial concentration of HCl in the acidic solution is set to correspond to the final concentration of HCl in the discharge phase. Consequently, the acid and base concentrations should be roughly equal at the beginning and end of each cycle. The target acid concentration in the charge phase represents the maximum charge state of the battery. Specifically, 0 M HCl corresponds to a state of charge (SoC) of 0%, and 1 M HCl corresponds to 100% SoC. The initial salt solution volume was set 6 times higher than those of the acid and base solutions to reduce NaCl concentration variations in the salt channels and thus prevent NaCl depletion during battery charging. The operating conditions and design features of the stack were already presented in detail in our previous work (Culcasi et al., 2022b).

In terms of performance indicators, the represents the energy obtained during the discharge of the battery per unit volume of electrolyte solution. Importantly, the energy spent for pumping the electrolyte solutions is taken into account in the calculation of the . The was calculated as follows:

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|  | (1) |

where is the number of triplets, and are the spacer width and length, respectively, is the discharge Gross Power Density, is the pumping power density, is the discharge duration and is the acid solution volume. The LCOS was calculated as follows (by assuming no financial amortization plan, no taxes):

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|  | (2) |

where is the Fixed Capital Investment, is the annual Operating and Maintenance cost, is the annual cost of electricity to charge the battery, is the energy collected yearly in the discharge battery phase, is the plant lifetime and is the discount rate. The economic parameters are reported in Table 1.

Table 1: Input parameters of the economic model.

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| Discount rate (*i*) | 8% |
| Electricity price | 0.05 € kWh−1 |
| Unitary Capex | 4,700 € kW−1 |
| Unitary Opex | 150 € kW−1 y−1 |
| Lifetime (*nyears*) | 10 years |
| Working time per year | 8,000 hours |

Particularly, the *Capex* depends on the nominal power of the battery, and it pertains to the first year of investment. In contrast, the *Opex* are annual. In the reference conditions, the cost of electricity is set at 5 €cents per kWh, based on renewable energy costs. Furthermore, across varying process conditions, there are different charging and discharging times. Thus, the total number of working hours was chosen rather than setting the number of cycles per year. The results of the TEA were presented using tornado diagrams, in which the efficiencies of the two battery phases were increased or decreased equally to impose an RTE change over the baseline by 20% in relative terms. In other scenarios, the plant lifetime, electricity price, capital cost and discount rate were altered by ±50% one by one.

* 1. Results and discussion

Figure 2a displays the NED plotted against the average NPD.

Figure 2: a) Net Energy Density and b) Levelized Cost Of Storage as functions *of the Average Net Power Density* in the discharge phase.

Figure 2a shows that the NED exhibits a non-monotonic trend with a minimum and a maximum at intermediate conditions. Therefore, the conditions that optimise the RTE or the do not correspond to the maximum nor minimum values of the NED. Specifically, the NED reaches its minimum value (~4.8 kWh m−3) at an of 7 W m−2 and its maximum value (~11 kWh m−3) at an of 16 W m−2. Therefore, maximising the RTE, which was an objective function leading to the lowest (Culcasi et al., 2022b) may result in the use of large volumes of electrolyte solutions, which would require a significant increase in the space occupied by the AB-FB system. Conversely, the volume of electrolyte solutions could be minimised by operating the battery at higher values but at lower energy efficiency. The low energy efficiency, in turn, would mean a reduction in the amount of energy recovered compared to that fed into the system. It is important to note that the NED values discussed in this study are the actual values obtained by the system rather than theoretical values, which would typically be higher. The efficiency of the discharge phase is influenced by the deviation of the actual NED from the theoretical values. In general, the discharge efficiency of the system exhibits variability along the Pareto curve, highlighting the trade-offs between different operating conditions and their effects on the overall performance of the AB-FB system.

Figure 2b illustrates the LCOS as a function of the along the Pareto curve. The figure shows that the LCOS increases monotonically from ~0.24 € kWh–1 to ~0.35 € kWh–1. Notably, operating at high (i.e., conditions that maximise NED) significantly increases the LCOS. The minimum and maximum points of NED correspond to changes in the slope of the LCOS profile, which divides the curve into three segments. This fact is determined by the value of the decision variables resulting from the optimisation problem, with the charge and discharge target concentration profiles being the primary contributors to this trend. The maximum NED corresponds to an LCOS of 0.32 € kWh–1, while operating at the minimum NED results in a reduction in the LCOS to 0.27 € kWh–1. It is important to note that the profiles in Figures 2a and b are not Pareto curves, as the optimisation was conducted with two objectives: the RTEnet and . A purposefully conducted optimisation study is necessary to obtain higher NED and lower LCOS values. However, the NED is linked to aspects beyond the economic ones, i.e. the practical problems of footprint.

The LCOS values shown in Figure 2b are the results of the economic model inputs listed in Table 1. However, these variables are subject to uncertainty; thus, a sensitivity analysis of the model is required to investigate the relative importance of these parameters individually. Figure 3 presents Tornado diagrams for the maximisation scenarios of either the RTE (corresponding to the minimum value of studied), graph a, or the , graph b, using the input parameters shown in Table 1 as a baseline.

Figure 3: Tornado diagrams of LCOS for a) RTEnet maximisation scenario and b) maximisation scenario.

The parameters are listed from top to bottom based on the decreasing order in the absolute variation in the LCOS. The battery lifetime is clearly the parameter with the greatest impact on costs. Reducing the lifetime from 10 to 5 years increases the LCOS by ~28%. On the other hand, extending the lifetime from 10 to 15 years results in a smaller reduction in the LCOS by ~12% in relative terms, regardless of the optimal point considered. Capital costs are more relevant when the net RTE is maximised, with an average variation of ±7 €cents kWh–1. When aiming to maximise the NPDd, the electricity price assumes a more crucial role. This can be ascribed to the direct association between electricity costs and the energy required for battery charging, which is generally greater in scenarios with high NED (see Figure 2a). Changes in the discount rate significantly affect the LCOS when maximising RTE (17% variation). Additionally, a 10% relative change in RTE has a the smallest effects in the LCOS.

* 1. Conclusions

In this study, we conducted a techno-economic analysis of an Acid/Base Flow Battery (AB-FB) with bipolar and monopolar ion exchange membranes. Optimal scenarios in terms of discharge Net Power Density and net Round-Trip Efficiency from a previous study were used to evaluate important performance parameters such as Net Energy Density (NED) and Levelized Cost of Storage (LCOS). Along the Pareto curve obtained by maximising the net RTE and NPD, the NED showed a non-monotonic behaviour, and its absolute minimum and maximum values did not coincide with the maxima of the objective functions. Conversely, the LCOS increased as a function of the NPD. Tornado diagrams showed that variations in lifetime led to a maximum LCOS variation of 31% compared to the reference value. Capital costs played a key role, causing LCOS variations of 7 €cent kWh–1 (20–30% in relative terms). Future research should aim to improve not only the RTEnet, , and NED, but also reduce LCOS while exploring different process configurations, such as open-loop and closed-loop systems. Moreover, it is essential to carry out studies using various membrane and stack designs in order to optimise the performance of the AB-FB. Additionally, the integration of batteries with renewable energy sources, such as solar and wind power, and their implementation in modern smart grids and districts should be thoroughly investigated. This comprehensive approach will be of great interest in advancing our understanding and application of energy storage technologies.

Nomenclature

– spacer width, m

– Fixed Capital Investment, €

– Annual electricity cost, €

– Annual discharge energy, kWh

– Gross discharge power density, W m–2

– discount rate, -

– generic year, y

– spacer length, m

– Levelized Cost Of Storage, € kWh–1

– Number of triplets

– Net Energy Density, kWh m–3

– Annual Operating and Maintenance cost, €

– Pumping Power Density, W m–2

– generic time, s

– discharge time, s

– acid solution volume, m3

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