Reactive Metals as Energy Carriers

An Aluminum-based Hybrid Energy Storage Case

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***Abstract*— Rapid acceleration on decarbonization of the major emitting sectors (i.e., energy generation, transportation) becomes more emergent to reach CO_2 mitigation targets. In this sense, installation of renewable energy technologies and ensuring its continuous availability are crucial aspect for the emission reduction. To maintain this, availability of storage technologies and renewable fuels must be ensured. Mainly, Power-to-X technologies enable the balance of generation using different energy vectors (chemicals, heat, gas, etc.). In that sense, hydrogen (H_2) is considered the main electricity-based fuel due to its large specific energy density. Nevertheless, techno-economic obstacles disabling its massive utilization necessitates the introduction of alternative energy carriers to meet the demand. For the very reason, metal energy carriers become very interesting alternatives for supporting this demand as they are energy dense heat and H_2 carriers Especially, metals like aluminium (Al), iron (Fe), sodium (Na) considering their wide availability. Thus, in this study an Al wet combustion plant and use case is presented for contemporaneous electricity (4 MW_e) and H_2 (up to 46.8 kg h^{-1}) supply aiming the mobility sector demand management and grid services. The proposed concept is a circular metal system where combusted Al is returned to the producers as Al_2O_3 and the round-trip efficiency of the system reaches up to 40.7% assuming a carbon-free Al smelting process. As for the economics, competitive electricity and H_2 costs are estimated with respect to other energy carriers. Especially, the Al-based H_2 cost which is in the range of 4.2–9.6 € kg^{-1} H_2 as discussed in detail.**

Keywords- aluminium; Power-to-X; hydrogen; electric mobility

I. INTRODUCTION

Alerting climate change impacts and reducing CO_2 budget of the Earth have been driving forces that accelerate the efforts given for a massive and rapid decarbonization of all sectors. Energy supply (including, industry, transport, and buildings) constitutes 73% of the global greenhouse gas emissions (GHGs), which have to be substituted by sustainable energy technologies in particular renewable energies [1]. As a result, demand on sustainable energy storage technologies and carriers are also significantly increased in parallel with the increasing share of renewables integrated in the grid [2]. Among all energy carriers, hydrogen (H_2) is considered as the most critical energy carrier as it has the highest gravimetric energy density. Nevertheless, high cost of electrolyzers and techno-economic -mainly due to very low volumetric energy density and high storage costs- obstacles encountered for its use in Power-to-X context hasten its overall use [3]. Hence, diversifying the energy carriers and increasing distributed energy storage is vital for the power supply security. Particularly, importance of alternative energy carriers that will adequately respond the energy storage demand has been once more highlighted due to the energy crisis that Europe has been experiencing since COVID-19 pandemic and new geopolitical challenges.

In this manner, all these obstacles brought the use of metals as energy carriers again on the table. Besides, their use in energy technologies, metals are energy carriers with high energy densities (both volumetric and gravimetric) [4]. Moreover, abundant metals such as aluminium (Al), and iron (Fe) are produced in large quantities with a long-term secured availability [5]. Especially, Al as a high energy dense metal appears to be a very advantageous energy carrier as it only requires electricity for major production steps as an energy source. In addition to that, it has a carbon-neutral production potential with the implementation of inert anode and drained cathode technology in the primary aluminium production process [6], [7].

Herein, considering all the sustainable renewable energy carrier requirements of the future energy grid, an aluminium-based hybrid energy storage technology is proposed as a solution for supplying electric and H_2 demand of the mobility sector and providing additional flexibility to grid [8], [9]. The proposed system is evaluated from a techno-economic perspective for a refueling station and storage business case as presented.

II. BACKGROUND – METALS AS COMBUSTIBLES

Besides metals being favorable electrochemical energy carriers, they can be considered as combustible fuels due to their high reactivity. In addition to that, once the metal is activated they can be easily oxidized using both water and oxygen in the air as an oxidizer. Nevertheless, not all the metals in the periodic table are suitable to be used as a combustible fuel. As summarized in the given overview in

Table 1, some metals e.g., Al, Fe, and Na are compatible energy carriers considering also the earth abundance and European supply security concerns in addition to advantageous volumetric energy densities [10].

TABLE I. ENERGY DENSITY AND SUPPLY ASPECTS OF REACTIVE METALS AND SEMI-METALS IN THE PERIODIC TABLE. [9]

Energy Carrier	***Gravimetric energy density [kWh kg^{-1}]***	***Volumetric energy density [kWh L^{-1}]***	***Earth abundance***	***Secured Supply***
B	16.4	38.3	☒	☑
Li	12.7	6.8	☒	☒
Al	8.6	23.5	☑	☑
Fe	2.1	16.7	☑	☑
Na	5.9	5.7	☑	☑
Mg	7.3	12.6	☑	☒
Si	9.1	22.5	☑	☒

As can be concluded from the given table above, Al demonstrates very motivating properties both in energy density and supply constraints as it can be easily recycled. Additionally, it is highly reactive and can be oxidized through the following oxidation reactions:

$$4\,Al + 3\,O_2 \rightarrow 2\,Al_2O_3 \quad \Delta H = -8.6\ \mathrm{kWh\ kg_{Al}^{-1}} \qquad (1)$$
$$2\,Al + 3\,H_2O \rightarrow 2\,Al_2O_3 + 3\,H_2 \quad \Delta H = -4.2\ \mathrm{kWh\ kg_{Al}^{-1}} \qquad (2)$$

The first reaction refers to direct oxidation of Al metal, and the second reaction expresses the wet-combustion path where it delivers 4.2 kWh kg^{-1}_{Al} heat and 0.111 kg H_2 (4.4 kWh kg^{-1}_{Al} heat equivalent). Though, the latter is more interesting for the hybrid energy storage use case where the designed business case will benefit from the H_2 carrier feature of Al.

In this study, an Al combustion plant presented using solid Al particles and steam for oxidation. The released heat and H_2 are then used for electricity and H_2 supply for mobility and the grid via the Al combustion plant situated in a refueling station. The business case is based on a sector coupling between Al producers and refueling station operators where Al is purchased from the producers (with a reduced prices) and combustion product Al_2O_3 is returned to producers for Al again through Hall-Héroult process.

In order to evaluate the business case a techno-economic evaluation model is developed based on the explained methodology in the following.

III. METHODOLOGY

A. *Technical Design and Evaluation Methodology*

A 0D process simulation model is developed for simulating an Al combustion system using a steam turbine for reactor cooling and a solid-oxide fuel cell (SOFC) which is connected to the system for the utilisation of H_2 and generating electricity with a design power of ~4 MW_e. In addition to that, a heat recovery section is thermally integrated to heat the compressed air required for the fuel cell to increase the thermal efficiency and a tail burner and gas turbine to utilize the excessive unreacted H_2 in the SOFC. Remaining waste heat is then used for preheating the feedwater as described in detail in [8].

Considering the designed business case, previous system design is modified to enable partial load operation of the SOFC and enable use of H_2 on demand. A H_2 compression section is also integrated to the system to allow flexible hybrid operation. (See Fig. 1).

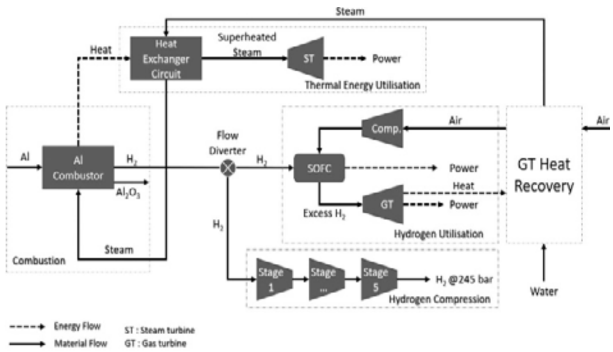

Figure 1. Simplified Al wet combustion plant layout showing main energy and material streams [9].

The developed system is then further optimized to determine efficient partial SOFC operation loads to maintain the operation temperature. Finally, the technical performance of the system is evaluated as presented.

B. *Economic Evaluation*

The provided system design is divided into its counterparts in order to estimate the required capital investment for building such a system. Design specification of each system component is obtained from the process simulation model as far as possible. The potential variations on the equipment specifications based on commercially available process equipment are also considered as uncertainties. Using learning curves the equipment cost of the system is estimated as explained in detail in [9]. Furthermore, installation cost, engineering, procurement and construction (EPC) costs and working capital are estimated using Guthrie's method [11]. The estimated direct and indirect investments costs hence constitute the depreciable capital expenditures (CAPEX) of the system. Considering an investment lifespan of 20 years, the estimated CAPEX is then depreciated using Modified Accelerated Cost Recovery System (MACRS) to determine the annual depreciation cost. For estimating the operational expenditures (OPEX), fixed and variable OPEX are classified based on the defined operation aspects in the technical design. These are fixed and variable O&M costs, fuel cost (net Al price) and transportation. Noting that, the net Al price refers to deducting Al_2O_3 economic value from the Al price as it is returned to the Al producers. Since it is a hybrid energy storage case, varying operation conditions (only electricity supply, or simultaneous electricity and H_2 supply) allocation of the CAPEX and OPEX needs a particular allocation to quantify the cost of the delivered energy. To do so, capital weighted cost allocation method is implemented in the economic evaluation to consider expenditures based on the operation modes. Consequently, with the aid of estimated CAPEX and implemented OPEX estimation methodology in the model levelized cost of electricity and H_2 (LCoE and

LCoH, respectively) are estimated across varying full load hours (FLHs) and scenarios. For a more detailed understanding on the economic model, the readers are referred to the published research article. (see [9])

IV. Results

A. Technical Evaluation Results

The defined system is simulated under variable operating modes and two partial operation modes are determined as optimized partial SOFC loads 65% and 80%. In other words, the SOFC below 65% partial load proves unstable efficiency dynamics due to non-uniform temperature distribution in the stacks. As limiting element is the SOFC, considering efficiency and hybridization constraints other energy conversion equipment (steam turbine (ST) and gas turbine (GT)) are also optimized accordingly. Technical performance evaluation at different partial operation modes are summarized in Table 2.

TABLE II. Plant power generation performance and H_2 production rate [9].

SOFC Part Load	*SOFC [kW]*	*GT [kW]*	*ST [kW]*	*H_2 Compressor [kW]*	*Total Power [MW]*	*H_2 Flow Rate [kg h^{-1}]*
100%	2000	906	1064	0.0	3.9	-
80%	1600	683	916	53.2	3.1	28
65%	1300	884	884	89.0	2.6	46.8

Therefore, based on these limits the system can be operated efficiently providing a certain flexibility depending on the H_2 production rate and electricity demand. For the defined operating points, the Al-to-Power efficiency ($\eta_{Al\text{-}P}$) values are determined in the range of 54-81% decreasing in parallel with the SOFC partial load. However, the overall Al-to-X efficiency ($\eta_{Al\text{-}X}$) of the system increases up to 93%. Meaning, increased H_2 production increases the Power-to-X conversion efficiency. As in this case Al serves as a renewable energy storage medium, another important technical performance parameter is the round-trip efficiency (η_{RTE}) which expresses the overall efficiency considering the necessary amount of energy to produce Al. Assuming an Al production energy intensity of 11 kWh kg^{-1}_{Al}, the η_{RTE} of the entire concept ranges between 35.6% and 40.7%, inversely related with the SOFC partial loads.

B. Economic Evaluation Results

Using the previously explained methodology, the baseline specific system cost is estimated as 5250 € kW^{-1} (lower:4200 – higher: 6200 € kW^{-1}). As for OPEX, putting all the operational aspects together, the described economic evaluation model is used for estimating the cost of the provided energy for the varying operational points. As a base case an electricity price 50 € MWh_e^{-1} is considered for Al production, the LCoE and LCOH are estimated as shown in Figure 2.

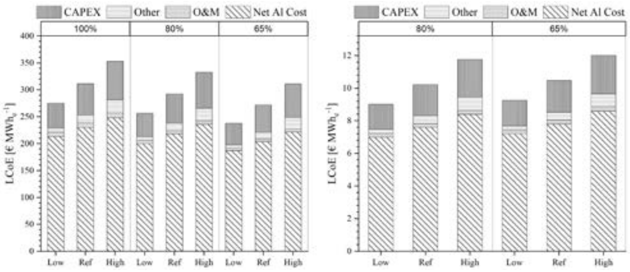

Figure 2 LCoE and LCoH estimations for the base case, i.e., 4000 FLHs and electricity price of 50 € MWh_e^{-1} under varying operation modes (100%, 80%, and 65% SOFC partial load) (Low: lower end, Ref: reference, and High: higher end.) [9].

Hence, the estimated LCoE and LCoH indicate that it is possible to provide electricity at a cost of 238-353 €/MWh_e^{-1} and H_2 ranging from 9 to 12 € kg^{-1} H_2. To further evaluate the cost reduction potential three scenarios concerning variable electricity prices, Al prices, and energy intensities are considered as follows:

- Scenario-I: Average Al price 1.65 € kg^{-1}_{Al}, Al smelting energy intensity 14.25 kWh kg^{-1}_{Al}, electricity price 50 € MWh_e^{-1}. This scenario aims to simulate the system using actual parameters.
- Scenario-II: Assuming an average Al price 1.26 € kg^{-1}_{Al}, Al smelting energy intensity 11 kWh kg^{-1}_{Al}, electricity price 30 € MWh_e^{-1} to simulate the system for near future parameters.
- Scenario-III: This scenario considers an average Al price 0.93 € kg^{-1}_{Al}, Al smelting energy intensity 11 kWh kg^{-1}_{Al}, electricity price 0 € MWh_e^{-1} to determine the lowest extreme economics limits.

Considering the above introduced scenarios, the economic evaluation model is run for 1000 – 8760 annual FLHs (11-100% capacity factor equivalent). As somewhat expected both LCoH and LCoE are showing decreased energy costs with reduced flexibility as shown in Figure 3.

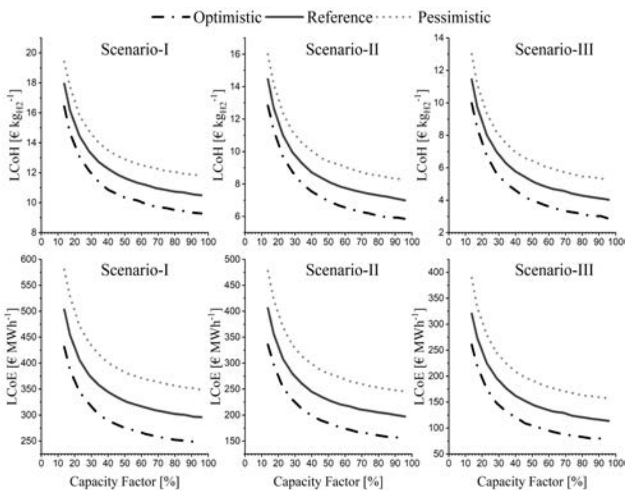

Figure 3 Variation of LCoE (PtP conversion) and LCoH (net fuel production cost) for the selected scenarios across all annual equivalent full load hour operations [9].

To sum up, Scenario-I proves relatively high electricity and H_2 costs but Scenario-II implies that it is possible to produce

30% cheaper electricity and H_2 if required conditions are maintained. As an extreme case, if the electricity is supplied free of charge (Scenario-III), a cost reduction on both LCoE and LCoH are estimated approximately 55%. All these scenarios are highlighting the fact that the potential of the concept is highly dependent on electricity prices.

V. CONCLUSION AND DISCUSSION

All in all, the techno-economic evaluation results indicate a business case development potential considering the estimated electricity and H_2 costs. In particular, the on-site production and consumption of H_2 bring numerous advantages to avoid large H_2 storage and transportation demand. To make a decent comparison, some renewable fuels are selected for comparison where Al based H_2 even with today's energy intensity and energy prices demonstrates high competitivity as illustrated in Figure 4.

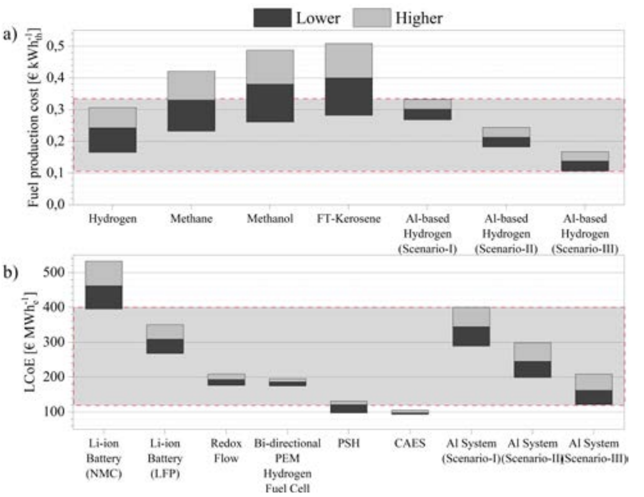

Figure 4 a) Comparison of net fuel production costs based on 4000 FLHs, and b) LCoE of various storage technologies based on power-to-power conversion path. (The power capacity of the selected technologies for comparison is 100 MWe and estimated LCoE values are based on the assumed 10 h of daily storage duration.) FT Kerosene: Fischer–Tropsch-synthesis kerosene, NMC: nickel–manganese–cobalt, LFP: lithium–iron–phosphate, PSH: pumped storage hydropower, CAES; compressed air energy storage.) [9].

As for electricity prices, in comparison with several battery technologies, the proposed system with the reduced electricity prices (starting from Scenario-II) displays high potential for further consideration. Especially, with respect to the PEM FC/ Electrolyzer combination with salt cavern storage, cost competitiveness of Al and on-site operation could make the concept more attractive. It is important to mention that increased share of renewables will yield more frequent price reductions (even negative electricity prices) that will create an arbitrage market with higher profit expectations. But only an electricity price of 30 € MWhe^{-1} already makes Al a high potential renewable energy carrier. Moreover, implementation of the inert anodes and drained cathodes will be sufficient for eliminating the direct emissions once 100% renewable electricity is used for the Al production. Also, produced Al can be considered as secondary as the Al_2O_3 returned to the smelter Al which will not increase demand on bauxite and Al will be used repeatedly. Another potential improvement, could be using low grade Al where the electricity consumption is reduced. However, a life-cycle assessment of the entire concept is a necessity for certain statements about its sustainability. Also, in framework of ALU-STORE project to utilize the high energy density of the Al metal additionally another energy conversion path (i.e, electrochemical) is being investigated for a seasonal energy storage case employing a mechanically rechargeable Al-air battery. The project aims to reach higher round-trip efficiencies. Eventually, the project outcomes will enable to make a comparison between electrochemical and thermochemical conversion pathways.

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REFERENCES

[1] H. Ritchie and M. Roser, "CO_2 and Greenhouse Gas Emissions," *Our World in Data*, 2020.

[2] "Energy Storage – Analysis," *IEA*. https://www.iea.org/reports/energy-storage (accessed Mar. 26, 2022).

[3] M. F. Ruth *et al.*, "The Technical and Economic Potential of Hydrogen within the United States," Research Org.: National Renewable Energy Lab. (NREL), Golden, CO (United States), Sep. 2021. [Online]. Available: https://www.osti.gov/biblio/1823433

[4] J. M. Bergthorson, "Recyclable metal fuels for clean and compact zero-carbon power," *Progress in Energy and Combustion Science*, vol. 68, pp. 169–196, Sep. 2018, doi: 10.1016/j.pecs.2018.05.001.

[5] M. Baumann, L. Barelli, and S. Passerini, "The Potential Role of Reactive Metals for a Clean Energy Transition," *Advanced Energy Materials*, p. 2001002, 2020.

[6] ELYSIS, "Rio Tinto and Alcoa announce world's first carbon-free aluminium smelting process," *ELYSIS*, Apr. 01, 2019. https://www.elysis.com/en/rio-tinto-and-alcoa-announce-worlds-first-carbon-free-aluminium-smelting-process (accessed Mar. 03, 2021).

[7] Y. He, K. Zhou, Y. Zhang, H. Xiong, and L. Zhang, "Recent progress of inert anodes for carbon-free aluminium electrolysis: a review and outlook," *J. Mater. Chem. A*, vol. 9, no. 45, pp. 25272–25285, 2021, doi: 10.1039/D1TA07198J.

[8] L. Barelli *et al.*, "Reactive Metals as Energy Storage and Carrier Media: Use of Aluminum for Power Generation in Fuel Cell-Based Power Plants," *Energy Technology*, vol. 8, no. 9, p. 2000233, 2020, doi: https://doi.org/10.1002/ente.202000233.

[9] H. Ersoy *et al.*, "Hybrid Energy Storage and Hydrogen Supply Based on Aluminum—a Multiservice Case for Electric Mobility and Energy Storage Services," *Advanced Materials Technologies*, Jan. 2022, doi: 10.1002/admt.202101400.

[10] European Commission, "Critical Raw Materials Resilience," European Commission, Website COM/2020/474, Sep. 2020. Accessed: Jan. 11, 2021. [Online]. Available: http://op.europa.eu/en/publication-detail/-/publication/160da878-edc7-11ea-991b-01aa75ed71a1/language-en/format-PDF

[11] D. J. Brennan, *Process industry economics: principles, concepts and applications*, Second edition. Amsterdam: Elsevier, 2020.