

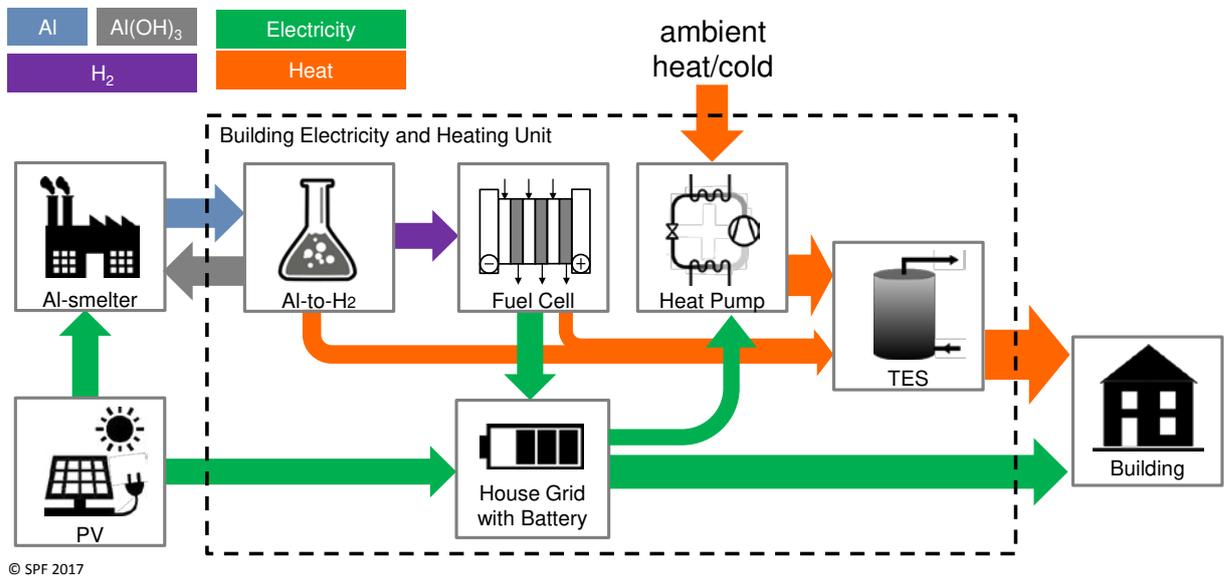


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# Applied Research

## HePoStAl

### Heat and Power Storage in Aluminum





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## Zusammenfassung

Es wurde eine Machbarkeitsstudie durchgeführt zur Beurteilung der Möglichkeit, mit Hilfe eines Aluminium Redox-Zyklus Energie saisonal zu speichern. Zur Beladung des Speichers wird oxidiertes Aluminium mit Hilfe von überschüssigem Strom aus erneuerbaren Energien im Sommer in einer zentralen Aufbereitungsanlage reduziert in seine Grundform. Die Entladung erfolgt im Winter am Ort des Energiebedarfs, über eine Reaktion des Aluminiums mit Wasser. Diese Reaktion setzt Wärme, Wasserstoff und Aluminium-Hydroxid oder Aluminium-Oxid frei. Der Wasserstoff kann zum Zeitpunkt der Speicher-Entladung sofort in einer Brennstoffzelle umgesetzt werden zu Strom und Wärme.

Betrachtet wurde dieser Pfad der Energiespeicherung als Ergänzung eines Energiesystems für ein Einfamilienhaus, welches zu 100% mit Solarenergie versorgt werden soll. Die gebäudeintegrierte Photovoltaik liefert während des grössten Teils des Jahres in Kombination mit einer Wärmepumpe und konventionellen Kurzzeitspeichern sowohl Strom als auch Wärme für das Gebäude. Im Sommer werden Stromüberschüsse an eine zentrale Anlage geliefert, welche Aluminium zur saisonalen Speicherung regeneriert. Dieses Aluminium wird ans Gebäude zurück geliefert, und dort im Winter oxidiert, und der entstehende Wasserstoff in einer Brennstoffzelle umgesetzt. Sowohl die dabei entstehende Reaktionswärme als auch die produzierte elektrische Energie werden verwendet, um den nicht durch die Photovoltaik abgedeckten Winterbedarf für Strom und Wärme des Gebäudes zu decken.

Die Abklärungen haben ergeben, dass die chemischen Teilschritte des Aluminium-Zyklus im Labormassstab bereits realisiert und demonstriert worden sind, und dass sowohl die Ökobilanz als auch die Kostenbetrachtung positiv sind. Die Herausforderung wird darin bestehen, die im Labor demonstrierten Teilschritte der Aluminium-Hydrolyse und der Reduktion von Aluminium mit Inert-Elektroden weiter zu optimieren für einen kontrollierbaren kontinuierlichen Betrieb oder Batch-Prozess, welcher als Grundlage für den Bau von Prototypen dienen kann, die im Feld eingesetzt werden können.

## Résumé

Une étude de faisabilité a été réalisée pour évaluer la possibilité d'un stockage saisonnier de l'énergie à partir d'un cycle redox aluminium. Pour recharger le réservoir de stockage, l'aluminium oxydé est réduit à sa forme de base dans une usine de traitement centrale à l'aide de surplus d'électricité provenant des énergies renouvelables en été. Le déchargement s'effectue en hiver sur le lieu de la demande énergétique, par une réaction de l'aluminium avec l'eau. Cette réaction libère chaleur, hydrogène et hydroxyde d'aluminium ou oxyde d'aluminium. Au moment de la décharge du réservoir de stockage, l'hydrogène peut être immédiatement converti en électricité et en chaleur dans une pile à combustible.

Ce cheminement de stockage d'énergie a été considéré comme un complément au système énergétique d'une maison unifamiliale, qui doit être alimentée à 100% en énergie solaire. Le photovoltaïque intégré au bâtiment, en combinaison avec une pompe à chaleur et des systèmes conventionnels de stockage à court terme, fournit de l'électricité et de la chaleur au bâtiment pendant la majeure partie de l'année. En été, les surplus d'électricité sont livrés à une centrale qui régénère l'aluminium pour le stockage saisonnier. Cet aluminium est retourné dans le bâtiment, où il est oxydé en hiver et l'hydrogène qui en résulte est



transformé en pile à combustible. La chaleur de réaction et l'énergie électrique produite sont utilisées pour couvrir les besoins en électricité et en chaleur du bâtiment, qui ne sont pas couverts par le photovoltaïque.

Les investigations ont montré que les réactions chimiques du cycle de l'aluminium ont déjà été réalisées et démontrées à l'échelle du laboratoire et que l'analyse du cycle de vie et l'évaluation des coûts sont positives. Le défi consistera à optimiser encore davantage les sous-étapes de l'hydrolyse de l'aluminium et la réduction de l'aluminium à l'aide d'électrodes inertes démontrées en laboratoire dans le cadre d'un procédé continu ou discontinu contrôlable, qui peut servir de base à la construction de prototypes pouvant être utilisés sur le terrain.

## Summary

A feasibility study was carried out to assess the possibility of seasonal energy storage using an aluminum redox cycle. To charge the storage, oxidized aluminum is reduced to its basic form in a central processing plant with the help of surplus electricity from renewable energies in summer. Discharge is carried out in winter at the place of energy demand, through a reaction of aluminum with water. This reaction releases heat, hydrogen and aluminum hydroxide or aluminum oxide. At the time of storage discharge, the hydrogen can be immediately converted into electricity and heat with a fuel cell.

This path of energy storage was considered for an energy system for a single-family house, which is to be supplied with 100% solar energy. Building-integrated photovoltaics, in combination with a heat pump and conventional short-term storage systems, provide electricity and heat for the building during most of the year. In the summer, electricity surplus is delivered to a central plant that regenerates aluminum from aluminum hydroxide for seasonal storage. This elementary aluminum is returned to the building, where it is oxidized in winter and the released hydrogen is converted in a fuel cell. Both, the reaction heat generated and the electrical energy produced, are used to cover the winter demand for electricity and heat of the building, that remains after priority has been given to direct supply from PV, heat pump and storage.

The chemical steps of the aluminum redox cycle have already been carried out and demonstrated on a laboratory scale at different institutes. The investigations carried out in this current project have shown that both the life cycle assessment and the cost evaluation of the proposed system are positive. The challenge will be to further optimize the sub-steps of aluminum hydrolysis and the reduction of aluminum with inert electrodes demonstrated in the laboratory for a controllable continuous operation or batch process, which can serve as a basis for the construction of prototypes that can be used in the field.



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## List of abbreviations

BMW	Bayerische Motoren Werke
cr	crystalline
CAES	Compressed Air Energy Storage
CED	Cumulated Energy Demand
DHW	Domestic Hot Water
ENTSO-E	European Network of Transmission System Operators for Electricity
EU	European Union
g	gaseous
GWP	Global Warming Potential (IPCC 500 years)
IPCC	Intergovernmental Panel on Climate Change
l	liquid
LCA	Life Cycle Assessment
NR	Non-Renewable
PCM	Phase Change Material
PEM	Proton Exchange Membrane
PSI	Paul Scherrer Institut
PV	Photovoltaic
s	solid
SFH	Single Family Home
SH	Space Heat
SOFC	Solid Oxide Fuel Cell
TES	Thermal Energy Storage
US DOE	US Department of Energy
VW	Volkswagen



## 1 Introduction

The Swiss Energy Strategy 2050 foresees that the energy consumption per person shall be reduced by 13% for electricity, and by 43% for total consumed energy, compared to the status of 2000. The capacity for the production of renewable energies from other sources than hydro shall be increased by a factor of 2.6 from 4'400 GWh/a to 11'400 GWh/a. The Swiss people has confirmed this Energy Strategy with a popular vote on May 21, 2017, and the corresponding law will enter into force on Jan. 1, 2018.

While being a positive signal, it is clear that these goals will not be sufficient for the mitigation of climate change and to reach the target of keeping global warming below 2 K on average. More efforts and more stringent targets will be needed for the period after 2035. Solar energy is expected to contribute significantly to the decarbonization of the production of electricity and heat. However, being abundantly available in summer, and scarce in winter when more energy is needed to supply heat for space heating, the potential of solar energy utilization is hindered by a lack of suitable, energy and cost efficient, seasonal storage technologies.

Pumped hydro storage is currently the only technology on the market with a potential to store large amounts of energy cost effectively over time periods of several months. However, the increase of hydro-storage and electricity transfer capacities is confronted with large resistances against such large projects with considerable visible impact on the landscape and possibilities are therefore limited.

For storing heat large water storage tanks are a possible solution. The limited storage capacity of this solution calls for large storage volumes, which are not always available or only available at a certain price. Therefore, although this technology is a mature and well proven solution, it is only suitable for a niche market where the occupied volume is not of great importance. Large pit storages and ground probe storages have considerable better cost efficiency, but they are only applicable for storing heat in district heating networks, and district heating is currently only reaching 2% of the heated floor area of Switzerland.

All thermal heat storage technologies that are operated at relatively low temperatures have the disadvantage that they cannot be used for the production of electricity effectively. These storages are therefore not contributing to a seasonal storage of electricity. Furthermore, the volumetric heat storage density is usually orders of magnitude lower than for heating oil or other fossil or biomass fuels that currently cover a large share of the heat demand in winter.

What if a seasonal energy storage technology would be available that would allow for storing renewable energy with a storage density that is comparable or higher than that of heating oil, and that is able to provide both, heat and electricity?

With the process that is shown in Figure 1 it seems realistic to achieve this goal. This process is based on the chemical reaction of solid aluminum and (gaseous) water. The reaction of aluminum with water is used to discharge the storage by producing hydrogen, aluminum-hydroxide, and heat.



The hydrogen can be used in a fuel cell to produce electricity and again heat. With this cascade process, assuming a conversion yield of 100%, 1 kg of aluminum can be used to produce 2 kWh of electricity and 6 kWh of heat. Thus, the storage density of aluminum is 8 kWh/kg or 21'600 kWh/m<sup>3</sup>, which is a factor of two higher than the volumetric energy storage density of heating oil.

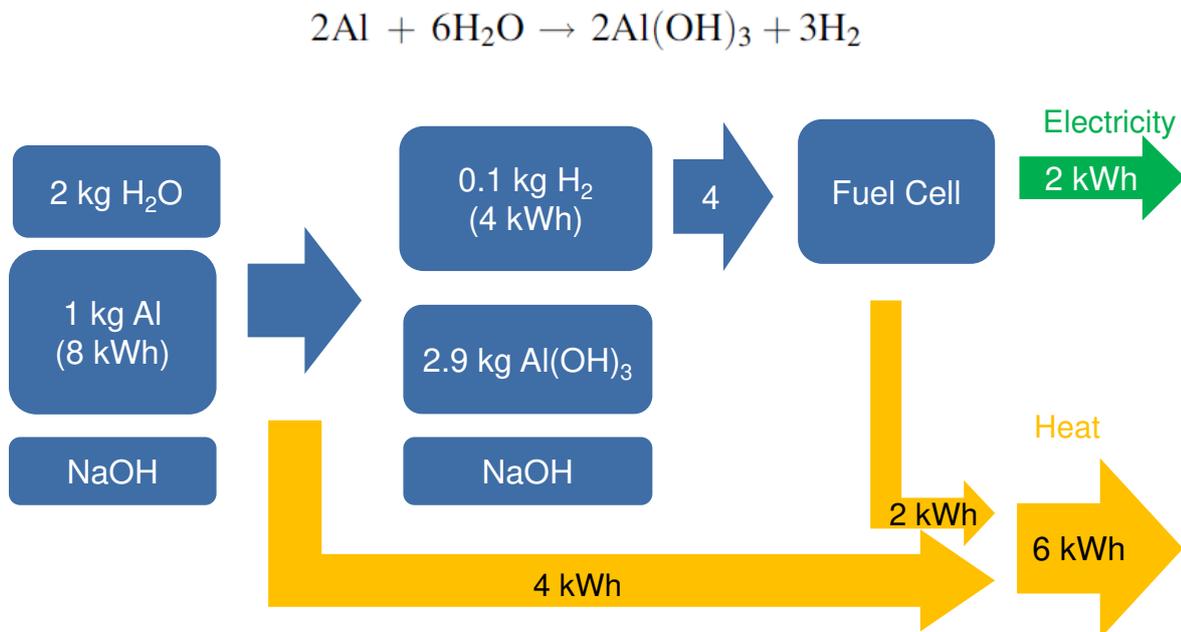


Figure 1: Producing heat and electricity from the oxidation of aluminum.

The process that is shown in Figure 1 can be carried out in single or multifamily buildings where the heat and electricity demand is to be covered. Fuel cells are already being installed in residential buildings for the provision of electricity and heat, and the oxidation of aluminum is a process that can be carried out at ambient temperature and pressure in alkaline solutions.

The largest challenge for this energy supply concept is most likely closing the cycle. The reduction of oxidized aluminum to the metallic uncharged state is a process that is currently carried out by the metal industry on a big scale with the Hall-Héroult process for the production of pure metallic aluminum from aluminum ore such as Bauxite with the help of electric energy. This process is certainly not suitable for the application in residential buildings. Furthermore, due to the carbon electrodes that are consumed or burned and converted into CO<sub>2</sub> in this process, it leads to emissions of non-renewable CO<sub>2</sub> that have to be included in the life cycle assessment of the full energy storage and discharging cycle.

This work investigates the possibility and feasibility of the process for seasonal heat and electricity storage shown in Figure 1, including the closing of the cycle that would need a breakthrough in research and development for processes and ways to reduce the CO<sub>2</sub>-emission of the Hall-Héroult process. Based on these results we are presenting simulations for a system concept that is able to supply a single family or multifamily building with 100% renewable energy based on solar energy and aluminum seasonal storage, and estimate the storage capacities and different variants for combining this process with photovoltaics, solar thermal heat,



and optionally ground or ambient heat in combination with heat pumps, and determine financial and environmental cost (LCA).

## 2 Methods

The methods applied are:

1. Literature study and expert talks, review of the state of the art of each of the components of the envisaged system.
2. Calculation and simulation of annual energy balances for electricity and heat for single and multifamily homes on the base of the envisaged system variants with and without solar thermal heat and with or without heat pumps.
3. Estimation of cost of the system components as far as information is available and the technology readiness level is at a high level.
4. Working out a project plan for demonstrating the feasibility of single components and combination of components in the lab.

## 3 Literature Review of the State of the Art

### 3.1 Energy Storage in Aluminum

Aluminum is an interesting material for energy storage because of its high energy storage density per volume which is higher than that of all other non-toxic metals and higher than oil, hydrogen or methane (Figure 2). The storage capacity of aluminum per volume is about two times the storage capacity of heating oil, and nine times the storage capacity of liquid hydrogen.

The main advantages associated with the use of aluminum as an energy storage are:

- very high energy storage density, both by weight and even more by volume
- unproblematic storability and transportability
- abundantly available in the earth's crust (third most frequent element)
- relatively low cost and well-known

The idea to use the oxidation and reduction of aluminum for the purpose of energy storage is not new. In 2004, PSI wrote a report for the Swiss Federal Office of Energy summarizing the advantages and disadvantages of aluminum as a fuel for combustion and as energy storage, and envisaged the use of renewable energies for the production of aluminum (Wochele & Ludwig 2004). This report summarized the state of the art in the thermochemical discharge, i.e. combustion of aluminum, where PSI had previously performed experiments from 1982 – 1991, and to some lesser extent also for the reduction of aluminum using inert electrodes. Although the possibility of producing hydrogen from aluminum was mentioned, the main focus was on the combustion of aluminum powder for co-generation. The authors recommended to further investigate the possibilities to use aluminum as an



alternative for hydrogen storage, and to support activities for research in this direction. A review article on different ways of using aluminum as an energy carrier and storage has been presented by Shkolnikov et al. (2011).

Because of its very high energy storage density, aluminum has been discussed and tested as an energy storage and hydrogen source for feeding fuel cells for the propulsion of marine vessels. Gany et al. (2015) demonstrated this applicability with model boat that ran for 40 minutes with 5 gram of activated aluminum powder as energy source.

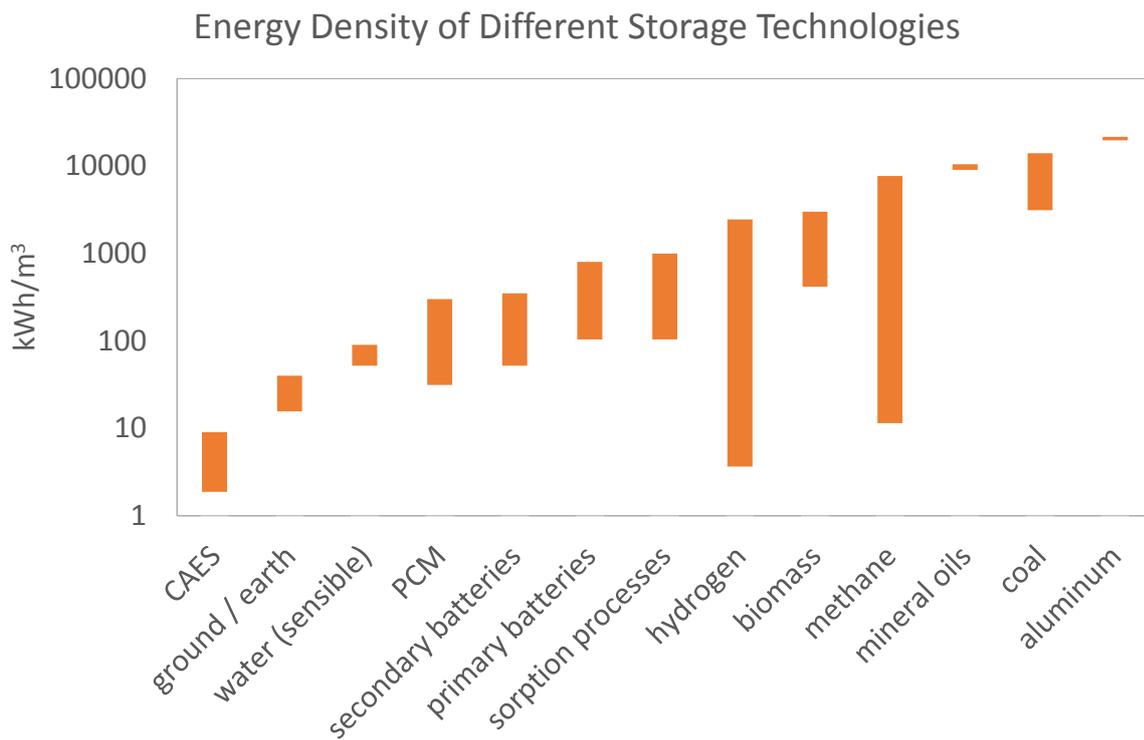


Figure 2: Volumetric energy densities of different storage technologies on a logarithmic scale. Reactants that are readily available such as air/oxygen or water are not included, neither are the reaction products. CAES = Compressed Air Energy Storage, PCM = Phase Change Material



Figure 3: Model boat for the demonstration of hydrogen produced from aluminum in combination with a fuel for the propulsion of marine vessels by Gany et al. (2015).



### 3.2 Production of Hydrogen from Aluminum

Aluminum reacts with water to form hydrogen and aluminum based compounds with different level of hydration, depending on the reaction temperature (*Eq. 1 - Eq. 4*). Aluminum hydroxide  $\text{Al}(\text{OH})_3$ , known also as bayerite is the stable product until  $280^\circ\text{C}$  (*Eq. 1*). Aluminum oxide hydroxide or boehmite (*Eq. 2*) is the stable form in the temperature range  $280^\circ\text{C}$  to  $480^\circ\text{C}$ , while for higher temperature aluminum oxide (alumina, *Eq. 3 + Eq. 4*) is the most stable (Belitskus 1970; Miller & Navarro 1996; Franzoni et al. 2010). For each of these reactions, the same amount of hydrogen is produced, only the required quantity of water, the form of the oxidized aluminum and the enthalpy of reaction are different.



These reactions are thermodynamically favorable from room temperature until aluminum melting temperature. For calculating the enthalpy of reaction of the processes involved in the HePoStAl project, the formation enthalpy of  $\text{Al}(\text{OH})_3$  was needed. This was found to be in the range of  $-1290 \text{ kJ/mol}$  ( $\Delta H_{f, 298}$ ). However the reference thermodynamic data are scarce and the values slightly differ (Belitskus 1970; Petrovic & Thomas 2008; Nie et al. 2012). From the reaction enthalpies ( $\Delta H_{r, 298}$ ) it can be seen that the reaction according to *Eq. 2* and *Eq. 3* produce more heat than the reaction according to *Eq. 1*, while they produce the same amount of hydrogen from a given quantity of aluminum. The difference between *Eq. 4* and *Eq. 3* is only the thermodynamic state of the water that enters the process in its gaseous (g) or liquid (l) state. Starting from liquid water, using heat recovery from the heat of reaction to evaporate it before it is reacting according to *Eq. 3*, the net heat production of this process will be lower than for the other three reactions. On the other hand, the advantage of this process is that the product is alumina which can be used directly for an aluminum smelter process without the intermediate step of calcination that is needed to turn aluminum hydroxide into alumina.

In general, the oxidation of aluminum to aluminum hydroxide is strongly exothermic, and the heat produced is just about equal to the energy content of the produced hydrogen<sup>1</sup>. Using excess water is necessary as the product  $\text{Al}(\text{OH})_3$  partially absorbs water to form hydrates/gel (Elitzur et al. 2014). Because aluminum surfaces oxidizes rapidly in contact with air or water, and the oxide layer is passivating the surface, the production of hydrogen is hindered under normal ambient conditions and in neutral water.

A review of aluminum for hydrogen production was given by Wang et al. (2009). Several methods have been investigated and applied successfully for the activation

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<sup>1</sup> It is assumed that the energy density of  $\text{H}_2$  is 40 kWh per kg  $\text{H}_2$ .



of passivated aluminum surfaces by removing the protective oxide or the produced hydroxide layer on the aluminum surface:

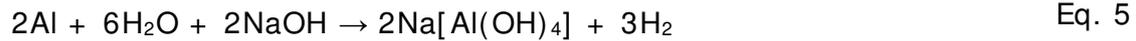
- Using an activator such as strong lyes (alkaline solutions): NaOH, KOH,  $\text{Ca}(\text{OH})_2$
- Grinding and milling aluminum just prior to the addition of water or while already mixed with water, possibly adding also salts (Alinejad & Mahmoodi 2009)
- Increasing the temperature to 200 – 300 °C and using water vapor to react with aluminum according to *Eq. 3*
- Using seawater with the addition of  $\text{NaAlO}_2$  (Soler et al. 2009)
- Using ultrasonic procedures for the preparation of the samples (Yang et al. 2014)
- Addition of Li-based (Elitzur et al. 2015) or choline hydroxide (Wang et al. 2017a) activators
- Carbon nanotube wrapping and treatment with infrared radiation (Zhang et al. 2017)

Elitzur et al. (2014) presented a method for the production of hydrogen from aluminum at ambient temperatures and pressures by adding a Li-based activator. The overall yield of produced  $\text{H}_2$  was similar for all the tested temperatures. The authors also combined this hydrogen producing unit with a Proton Exchange Membrane (PEM) fuel cell. In their experiments, they reached hydrogen production rates of 600 mL/min with a batch that contained about 20 mL of water and 2 g of aluminum, corresponding to about 130 W of energy transfer into hydrogen (based on its gross heating value). Thus, it seems to be realistic that production rates of more than 5 kW are possible with an Al-to- $\text{H}_2$  converter of the volume in the range of one to a few liters.

Soler et al. (2009) also report on hydrogen production rates of 700 mL/min with 100% yield for aluminum powder combined with seawater with the addition of  $\text{NaAlO}_2$ . They claim that a “synergistic effect of  $\text{Al}(\text{OH})_3$  suspensions in combination with  $\text{NaAlO}_2$  solutions was key in promoting Al corrosion”.

Remarkably, the simple addition of strong lyes and increase of temperature to 70 - 90 °C may already produce  $\text{H}_2$  at steady production rates and with a high yield. Since the reaction is exothermic, once the process has started it needs to be cooled rather than heated, and the heat that is transferred to the cooling medium can be used for heating e.g. a building or domestic hot water in winter. Special additives such as Li-activators and choline hydroxide are only needed if the corrosivity or hazards associated with strong lyes shall be reduced, or if the temperature needs to be decreased towards ambient temperature levels.

Using sodium hydroxide is an efficient and cost effective method to increase the hydrogen yield. Several authors reported that aluminum reacts with an aqueous solution of NaOH (*Eq. 5*) and that NaOH is regenerated (*Eq. 6*) by the precipitation of  $\text{Al}(\text{OH})_3$ , thus acting as a catalyst (Andersen & Andersen, 2002; Martínez et al. 2005; Soler et al. 2009).



Elsarrag et al. (2017) found that also heavily adulterated scrap aluminum, which is not suitable for recycling and secondary aluminum production can be used for hydrogen generation. However, aluminum alloy composition seems to have an impact on the hydrogen production rates.

Furthermore, the use of aluminum as a storage from which to produce hydrogen for a fuel cell for portable electronics has also been investigated and reported by a team of Samsung Electro-Mechanics in Korea (Jung et al. 2008).

### 3.3 Fuel Cells

For high-efficiency conversion of hydrogen to electricity, fuel cells are the state of the art. Different types of fuel cells for the conversion of hydrogen exist (Table 1). For the application in single and multifamily homes it is more convenient to use air as an oxidant rather than oxygen, and to work with temperatures of no more than about 100 °C. The only fuel cell type that fulfills both of these criteria is the Proton Exchange Membrane (PEM) fuel cell. This is at the same time the most widely used fuel cell today. For these reasons the focus in the following section is on the state of the art of this type of fuel cell, although also SOFC fuel cells could be an option and could turn a higher fraction of the hydrogen energy content into electricity.

*Table 1: Types of fuel cells for the conversion of hydrogen, source: Sterner & Stadler 2014 & Töpler & Lehmann 2014.*

<b>Type</b>	<b>Abbreviation</b>	<b>Oxidant</b>	<b>Temperature °C</b>
Alkaline Fuel Cell	AFC	O <sub>2</sub>	20 - 90
Molten Carbonate Fuel Cell	MC-FC	O <sub>2</sub> , air	600 - 650
Phosphoric Acid Fuel Cell	PA-FC	O <sub>2</sub> , air	160 - 220
Proton Exchange Membrane Fuel Cell	PEM-FC	O <sub>2</sub> , air	60 - 180
Solid Oxide Fuel Cell	SOFC	O <sub>2</sub> , air	800 - 1000

According to various sources, the theoretical efficiency of fuel cells is around 80%, however, in practical applications, efficiencies between 40 – 60 % are realistic. According to Mitzel & Friedrich (2016), Mitsubishi Hitachi Power systems has installed a 250 kW demonstration plant with an efficiency of 55% in Japan in 2015, and DLR (Germany) has announced to produce a 30 kW prototype fuel cell with an electric efficiency of around 60% in the coming years.

For stationary home applications, measured efficiencies have been reported as up to 33 % of the energy towards electricity and 96 % towards electricity and heat combined<sup>2</sup>. Therefore, the electric efficiency that can be expected from market

<sup>2</sup> <https://www.enbw.com/unternehmen/konzern/forschung/erneuerbare-energien/brennstoffzelle.html>, accessed on Aug. 28, 2017, and (Mitzel & Friedrich 2016).



ready products today is expected to be between 30 and 40%, with substantial potential for increasing efficiencies in the future.

PEM-FC for stationary applications are in competition with SOFC that faces less problems with impurities, especially CO, in the hydrogen carrying gas. For the envisaged application where hydrogen is not produced from hydrocarbon reforming but from the oxidation process of aluminum, the sensitivity of the fuel cell to CO is not expected to be crucial.

PEM-FC are the favorite technology today for automotive application, have therefore been investigated and developed with high efforts, and are a market available technology. For stationary applications in buildings, there are two branches: High-Temperature PEM that are operated at 160 – 180 °C, and Low-Temperature PEM that are operated at around 80 °C. According to Mitzel & Friedrich (2016), market readiness and reliability have been demonstrated in projects such as Callux in Germany. The main challenges are cost reduction, increase of electric efficiency, and total hours of operation without replacement of the fuel cell stack or its key components.

As a consequence, it can be said that fuel cell technology for the supply of buildings with electricity and heat is at the stage of market introduction, with already seven companies offering devices on the German market in 2017<sup>3</sup>:

- LT-PEMFC: Viessmann and SenerTec
- HT-PEMFC: Elcore
- SOFC: Vaillant, Buderus, Hexis and SolidPower

The US DOE 2016 reports that Panasonic launched a new Ene-Farm fuel cell system in Japan that has a durability of 70'000 hours and sells for around (\$12'700) before tax and installation by Tokyo Gas. More than 140'000 micro-CHP units with fuel cell technology have been sold and installed in Japan so far (US DOE 2016).

In the automotive industry, companies like Toyota, Hyundai, Honda, Audi, Mercedes, BMW and VW all already offer fuel cell vehicles that are produced in small series (Mitzel & Friedrich 2016). Most of them use PEM-FC technology in combination with Li-ion batteries. Several European cities already operate buses and utility vehicles based on fuel cell technologies. Fuel cells have been also tested for the application in rail transport and in planes, and an increasing number of forklifts are operated with fuel cells.

A number of companies also offer small PEM fuel cells in the range below and a few kW of power (Table 2).

*Table 2: small scale commercial PEM fuel cells (below to a few kW), according to US DOE (2016).*

<b>Company</b>	<b>Product</b>	<b>Power</b>
Nedstack (NL)	HP	2 – 10 kW (scalable)
	XXL	2 – 9.5 kW (scalable)
Panasonic (Japan)	Ene-Farm	200 – 750 W
Toshiba (Japan)	Ene-Farm	200 – 700 W
	H2One	N/A

<sup>3</sup> <http://www.ibz-info.de/modelle.html>, accessed on Aug. 28, 2017.



### 3.4 Closing the Cycle by Reduction of Aluminum

#### 3.4.1 Current Hall-Héroult process

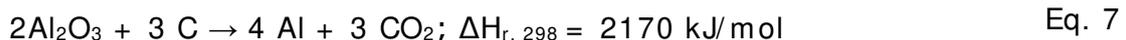
The current state of the art for aluminum production is the Hall-Héroult process that has been developed and patented in 1886. In this electrolyte or “aluminum smelting” process, aluminum oxide (alumina,  $\text{Al}_2\text{O}_3$ ) is dissolved in an electrolyte that contains molten cryolite ( $\text{Na}_3\text{AlF}_6$ ) at 960 °C. In the electrolyte process the main energy input is electricity that can be produced from renewable sources such as wind, hydro or photovoltaics. However, the downside of the energy and environmental balance of the process are the carbon electrodes that are produced from a mixture of petroleum coke and coal tar pitch binder.

Petroleum coke, also known as petcoke, is a solid carbon material, which can include a variety of elements and metals in a wide range of concentrations, obtained as a by-product of the oil refining process. Coal tar is obtained from the combustion of coal in absence of air in a process called destructive distillation of coal, in which coke is also obtained as a residual product of the combusted coal.

The electrodes made of petcoke and coal tar are consumed and converted into  $\text{CO}_2$  in the process, leading to a number of negative effects:

- The  $\text{CO}_2$  that is produced is from fossil sources and impacts negatively the climate warming impact even when the electricity is from renewable sources
- At the anodes also perfluorocarbon gases ( $\text{CF}_4$  and  $\text{C}_2\text{F}_6$ ) are produced. These may impact the environment more than the  $\text{CO}_2$  emissions if they are not retained, possibly reaching 2 kg  $\text{CO}_2$ -eq/kg Al <sup>4</sup>.
- The process to obtain the source material for the electrodes, i.e. petcoke and coal tar are not environmentally friendly.

The reaction to obtain pure aluminum in the Hall-Héroult smelter process can be summarized as follows:



For each ton of aluminum produced, around 400 kg of carbon and 13 – 15 kWh of electricity are consumed in this reaction<sup>5</sup>, leading to a GWP of 1.76 kg  $\text{CO}_2$  per kg of aluminum from the carbon electrode burning alone, plus additional emissions depending on the electricity source and energy used to produce the carbon electrodes, if upstream process emissions are accounted for.

Using heating oil for heat supply with an efficiency of 85% leads to 0.38 kg  $\text{CO}_2$ -eq. per kWh of heat produced. In comparison, the use of aluminum that is produced with the Hall-Héroult process would lead to emission of 0.22 kg  $\text{CO}_2$  per kWh<sup>6</sup>. These emission stem from the consumption of the carbon electrodes alone, upstream processes and losses not yet accounted for. Although the overall balance is still favorable in comparison to heating oil, in particular when also electricity can be produced and not only heat, the consumption of carbon electrodes in the Hall-

<sup>4</sup> <http://www.agral-project.com/the-agral-project/primary-aluminium-production/>

<sup>5</sup> AGRAL project 2017, Wochele & Ludwig 2004, Kvannd & Drabløs 2014, Worrell et al. 2007, Springer & Hasanbeigi 2016

<sup>6</sup> 1.76 kg/kg / (8 kWh/kg)



Hérault process must be eliminated if the GWP of the overall energy storage cycle shall be kept minimal.

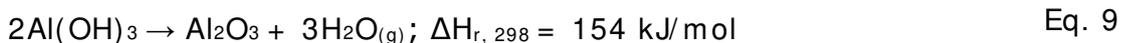
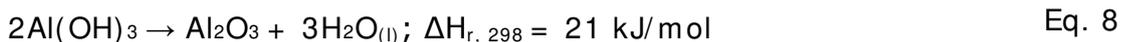
According to several sources, the overall energetic balance of the Hall-Hérault process is about 12.4 kWh of electricity plus 0.4 kg carbon (equals 3.8 kWh) for electrodes per kg of aluminum produced. From this, an overall efficiency of 65 % can be concluded if only electricity is accounted for, and 50 % including the energy content of the carbon electrodes. One of the world leaders in aluminum production, UC RUSAL, announced recently that they are able to reduce the electricity consumption down to 11.8 kWh<sub>el</sub>/kg of aluminum, thereby further increasing the energetic efficiency of this process (Gupta 2016).

Alumina is usually obtained from Bauxite ore, which is the world's primary source of aluminum, typically found in topsoil located in various tropical and subtropical regions. The chemical processed to produce 1 kg of alumina from Bauxite needs about 8 kWh of primary energy (AGRAL project 2017, Springer & Hasanbeigi 2016). This correspond to an equivalent of 1.6 kg emitted CO<sub>2</sub>. However, this effort only has to be made once, and not repetitively once the aluminum storage cycle process is running.

### 3.4.2 Process to obtain Alumina from Aluminum Hydroxide

In order to close the cycle from the reaction described in Eq. 1, alumina has to be obtained from aluminum hydroxide. Therefore, for the energy balance and LCA, the emissions and cost of producing alumina from Bauxite (Bayer process) have to be replaced with the impacts and cost that result from producing alumina from aluminum hydroxide.

Alumina (Al<sub>2</sub>O<sub>3</sub>) is obtained from Al(OH)<sub>3</sub> in a calcination process:



According to the enthalpy of reaction, 21 kJ/mol have to be invested if the water that is released can be condensed to its liquid state and the phase change heat recovered, and 154 kJ/mol have to be invested if this is not the case. This corresponds to 0.1 kWh/kg of aluminum for Eq. 8, and 0.8 kWh/kg for Eq. 9.

According to Springer & Hasanbeigi (2016), the energy used for this process in practice is around 0.83 kWh per kg alumina (Al<sub>2</sub>O<sub>3</sub>), which corresponds to 1.57 kWh/kg aluminum.

### 3.4.3 Overall process efficiency

The overall summary for the combination of the calcination process and the Hall-Hérault process, assuming best practice values and the today applied technology of carbon electrodes that are consumed during the process, is listed in Table 3. We



assume here that electricity for the smelter process and for the calcination is from renewable sources and thus CO<sub>2</sub>-emission free. If this would not be the case and electricity would be produced from coal power plants, CO<sub>2</sub> emissions would be a factor of 10 higher.

*Table 3: Energy intensity and CO<sub>2</sub>-eq. emissions for the production of aluminum from aluminum-hydroxide, per kg aluminum.*

<b>process</b>	<b>kWh</b>	<b>kg CO<sub>2</sub>-eq.</b>
calcination	0.8	
consumption of carbon electrodes	3.8	1.5 - 1.76
electricity for smelter process	11.8	
<b>total</b>	<b>16.6</b>	<b>1.76</b>

### 3.5 Potential for energy savings

Considering the fact that 8 kWh of energy can be released or recovered per kg of Al, the overall efficiency of the calcination and Hall-Héroult process according to current best practice is only 47%.

Some of the energetic savings potentials that are reported by Springer & Hasanbeigi (2016) are listed in Table 4.

*Table 4: Energetic savings potential in the aluminum production process according to Springer & Hasanbeigi (2016).*

<b>new technology</b>	<b>energetic savings</b>	<b>direct CO<sub>2</sub> emissions</b>
inert anodes	3-4%	100%
wetted cathodes	20%	
multipolar cells	40%	
ionic liquids	30-85%	

The figures reported in this table have to be taken with caution. Energetic savings of up to 85% are not possible if the efficiency of the process is already around 50%. It seems to be likely that the authors have mistakenly reported values as potential for energetic savings that are in fact potential for the reduction of losses.

According to Wochele & Ludwig (2004), inert anode technology could lead to an increase in the efficiency to 84%, corresponding to 11 kWh/kg aluminum.

#### 3.5.1 Carbon Electrodes from Renewable Sources

To produce carbon electrodes from renewable sources such as wood could decrease the GWP of the aluminum production, but it would not increase the energetic efficiency of the smelting and calcination process that would remain at 50%. Instead of being used for producing charcoal for the aluminum smelting, wood could also be used for producing electricity and heat directly in CHP plants



and this route of energetic use must be compared with the carbon electrode - aluminum route.

The production of charcoal from wood yields at maximum 40% (w/w) of coal per mass of wood. Taking into account the heating values of these two fuels, the production of charcoal may reach energetic efficiencies of up to 80%.

### 3.5.2 Inert Electrodes

If the anode of the aluminum smelter process would be made of an inert material that is not consumed or only consumed at very low rates during the process, the oxygen that is stripped from the aluminum would not be combined with carbon and produce CO<sub>2</sub>, but it would recombine to form O<sub>2</sub>:



This process would bring several advantages:

- No direct CO<sub>2</sub> emissions from the process
- Frequency for replacing the anodes could be reduced drastically and thus cost spared
- Higher overall energetic efficiency

In a loss free process, 3350 kJ/mol would have to be invested for the stoichiometric reaction according to Eq. 10, corresponding to 8.6 kWh/kg aluminum produced. According to Springer & Hasanbeigi (2016), energy savings of 3-4% can be realized with this modification, compared to the Hall-Hérault process. Furthermore, this step would open up opportunities for other energy saving measures such as multipolar cells that are not possible with the current carbon electrode process.

*Table 5: Minimum energy intensity for the production of aluminum from aluminum-hydroxide with inert electrodes, according to thermodynamic limits, per kg aluminum.*

<b>process</b>	<b>minimum kWh</b>
calcination	0.1
electricity for smelter process with inert electrodes	8.6
<b>total</b>	<b>8.7</b>



Three types of inert anodes have been proposed for aluminum production (Kvande & Drabløs 2014):

- ceramics – electrodes made from inorganic, non-metallic, solid material
- cermet – a mixture of metals and ceramics, e.g.  $\text{NiFe}_2\text{O}_4 + \text{NiO} + \text{Cu} + \text{Ag}$
- metal electrodes, e.g. alloys made of  $\text{Ni} + \text{Fe} + \text{Cu}$

A short summary of the advantages and disadvantages of all three types is given by Sadoway (2001). The challenge is to find a material that is cost-efficient and does not corrode significantly in the reaction solvent. Corrosion leads to frequent replacement (and cost) of the electrodes on the one hand, and to impurities from the corroded material in the produced aluminum on the other hand. The second problem is serious for the metallurgic industry that needs to deliver high quality construction material. However, it may not be important if aluminum is to be used as an energy carrier.

The advantages of inert anodes are obvious, and the aluminum industry has been working for decades to find suitable solutions. The company Infinium was apparently working on zirconium oxide anodes, Rusal has developed inert anode technologies and announced pilots to begin operation, and Alcoa has piloted inert anode technologies already in 2013 (Springer & Hasanbeigi 2016).

According to Kvande & Drabløs (2014), Alcoa's chief executive officer stated already in 2000 that "the science is proved, so we have an inert anode, but we have not proved the commercial aspects." Much work has been carried out since then.

Kvande & Drabløs also state that a totally inert anode is an illusion because of the aggressiveness of the electrolyte used in the process, but a wear rate of 10 mm/year would already be a great success and might be sufficient.

Despite the fact that most research in this field is probably done on a private company base and will most likely never be published due to proprietary reasons, several authors have also worked on this issue and published results or will publish results:

- Pawlek (2014) gives an overview of work published on inert anodes until 2013, focusing on cermets, especially  $\text{Cu}(\text{NiO}-\text{NiFe}_2\text{O}_4)$  in cryolite melts, and metal anodes, e.g. Ni-Fe alloys for lower temperature operation in KF-based electrolytes.
- The EU is currently financing the AGRAL project that aims for the development of inert anodes for aluminum production, under the Horizon 2020 research program (CORDIS 2017a).
- Just recently, the Patent US9551078 2017 was published by the Aluminum Corporation of China, describing an aluminum smelter process with inert anodes and an electrolyte  $\text{KF}-\text{NaF}-\text{AlF}_3$  at operating of 700-850 °C. The patent states that the quality of the aluminum product is not less than 99.7%, and the cell is free from emissions of carbon dioxide and perfluorinated compounds.



- Olsen & Thonstad (2016) report on a  $\text{NiFe}_2\text{O}_4$ -based cermet material with a wear rate of 0.12 – 0.20 cm/year when used as inert anode in a conventional electrolyte.
- Beck (2016) reports on a stable metal alloy anode in an eutectic  $\text{NaF-AlF}_3$  bath at about 750 °C, and promises a 20-fold decrease in cell volume and a specific energy consumption of 11 kWh/kg aluminum produced.
- Arctus Metals Ltd., based in Iceland, has produced pilot lab scale plants based on the Beck cell and announced to scale up to market relevant sizes and sell turnkey aluminum smelter units by 2020 (CORDIS 2017b).
- Other published work on inert anodes is available (Meyer et al. 2017; Liu et al. 2017; Vecchio-Sadus et al. 2016; Tarcy 2016).

### 3.6 Alternative reduction technologies

An alternative reduction technology is e.g. the carbothermic reduction process. However, this process leads to  $\text{CO}_2$  emissions that are 60% higher than for the conventional Hall-Héroult process (Kvande & Drabløs 2014). Therefore, this is not considered to be a viable option for a „carbon free“ seasonal storage technology.

## 4 Energy System based on Seasonal Storage in Aluminum

### 4.1 System

The application of seasonal energy storage in aluminum is reasonable if the heat produced by the aluminum hydrolysis and the fuel cell does not have to be considered as losses, but can be used. This is the case if electricity and heat – possibly also cooling – have to be provided for a building. We are proposing this solution for a 100% solar driven residential building. The building may be a single family or a multifamily building. From an economic perspective, the multifamily building may be more favorable because the investment cost per unit energy provided is expected to be much lower. However, for the sake of simplicity, available roof surface for PV, and smaller prototypes to start with, an exemplary calculation is done for a single family building in this chapter. In section 4.4.2, the cost calculations for multifamily buildings are presented. Figure 4 gives an overview of the energy and material flows in this system. PV electricity and ambient heat provide 100% of the needed energy inputs. PV electricity is used as much as possible directly for household appliances and for heating and DHW preparation by a heat pump. A small Li-ion battery and thermal water storage are used for short term energy storage in the range of days and possibly up to a week. These are included in the “Building Electricity and Heating Unit” depicted in Figure 4 and detailed in Figure 5. An air or ambient source heat pump is used for the production of DHW in summer and space heating in colder seasons.

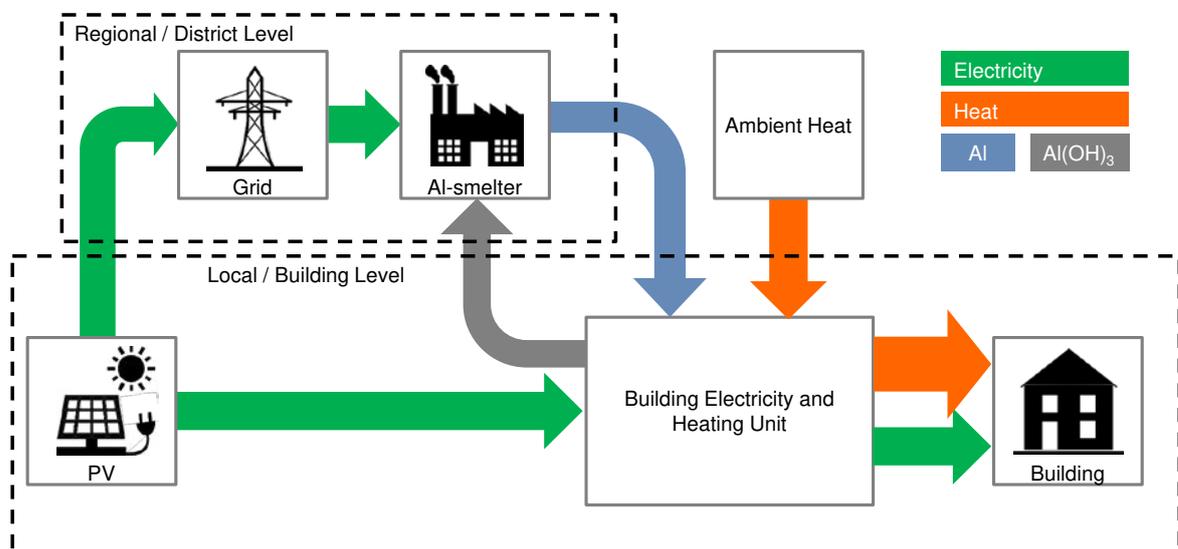


Figure 4: Energy system for 100% solar coverage of building heat and electricity based on PV and seasonal aluminum storage.

Only in winter, when PV yield is not enough, the aluminum hydrolysis process is started, producing heat and hydrogen. The latter is converted to electricity and heat in a fuel cell. At this point in the year, space heating demand is already substantial and the heat produced can be used 100%. For very cold days, the waste heat from the aluminum hydrolysis and fuel cell will not be enough and electricity from the fuel cell may also be used to produce additional heat by the



heat pump. The building electricity and heat unit therefore consists of the Al-to-H<sub>2</sub> converter, a fuel cell, a heat pump, and thermal (TES) as well as electrical (battery) storage (Figure 5).

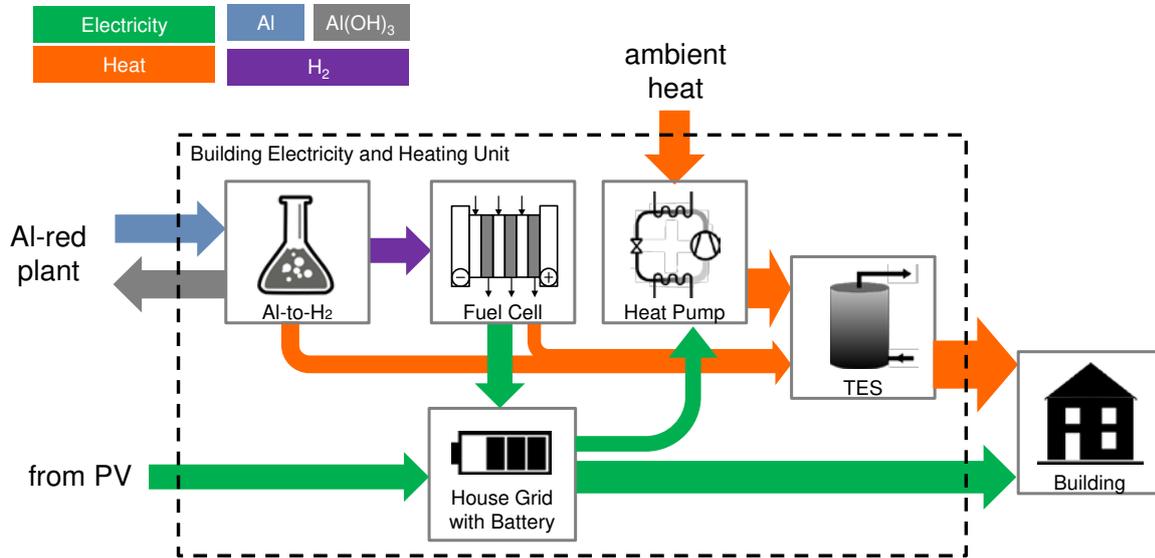


Figure 5: The building heat and electricity unit. TES = thermal energy storage, Al-red plant = aluminum reduction plant.

In the following, the electricity and heat demand of the single family building as well as the energy balances of the system are calculated and resulting energy balances are presented.

## 4.2 Methodology

An hourly calculation based on Excel was used to evaluate the yearly performance of the system. Weather data from the city of Zurich was used for a single family house with 140 m<sup>2</sup> heated floor area and a specific space heating and domestic hot water demand of 33 and 20 kWh/m<sup>2</sup> respectively.

The annual electricity demand was set to 24 kWh/m<sup>2</sup> floor area. Thus, the total building energy demand sums up to 11 MWh for heat and electricity combined.

Table 6: Specific and yearly demands for space heating, domestic hot water and electricity for a SFH.

	<b>specific demand<sup>7</sup></b>	<b>Total</b>
	<b>kWh/ m<sup>2</sup></b>	<b>MWh</b>
Space heating	33	4.62
Domestic hot water	20	3.08
Household electricity	24	3.36

<sup>7</sup> Demand per heated surface area



In order to assess the potential of the system from an energetic point of view, several efficiencies for the most important processes were modified. Three scenarios are considered:

- **Min:** this scenario represents today's average or documented practice.
- **Base:** this scenario represents today's best practice.
- **Max:** this scenario represents future possible developments.

Table 7: Assumptions for conversion efficiencies of single process steps, in %.

<b>Device</b>	<b>Process</b>	<b>min.</b>	<b>base</b>	<b>max.</b>
		<b>%</b>	<b>%</b>	<b>%</b>
Al-to-H <sub>2</sub> converter	Aluminum to hydrogen	40	45	49
Al-to-H <sub>2</sub> converter	Overall	80	90	98
Fuel cell	H <sub>2</sub> to electricity	35	50	60
Fuel cell	Overall	90	95	98
Al-Regeneration	Al(OH) <sub>3</sub> to Al	53	67	73

For each calculation the size of the PV field was adapted such that on a yearly base, the excess electricity from PV can produce enough Al to feed the Al-Regenerator. Thus, this excess PV electricity will be used to turn aluminum-hydroxide to aluminum in a central plant and store this aluminum for later use. The aluminum can be delivered to the buildings similar to today's delivery of fuels such as wood pellets or heating oil.

The size of the different components of the system installed at the building level are given in the following Table.

Table 8: Sizes of main components used for the provisions of heating and electricity in one SFH.

<b>Device</b>	<b>Size</b>
Al-to-H <sub>2</sub> converter	2 kW
Fuel cell	0.6 kW
PV	35-56-82 <sup>8</sup> m <sup>2</sup>
Heat pump	4 kW
Battery	10 kWh
TES	1 m <sup>3</sup>

<sup>8</sup> It depends of the assumptions of efficiencies described in Table 7 for Min, Base and Max scenarios.



### 4.3 Annual energetic balances

In order to illustrate the behavior of the system a monthly heating balance is shown in Figure 6, including the following energetic quantities:

- HpToDhw : heat provided from the heat pump to DHW
- HpToSh : heat provided from the heat pump to SH
- AlToHeat : heat provided from the Al-to-H<sub>2</sub> converter to the system (assumed to be delivered to the TES)
- Qdhw : domestic hot water demand
- Qsh : space heating demand
- QTesLoss : thermal losses in the TES

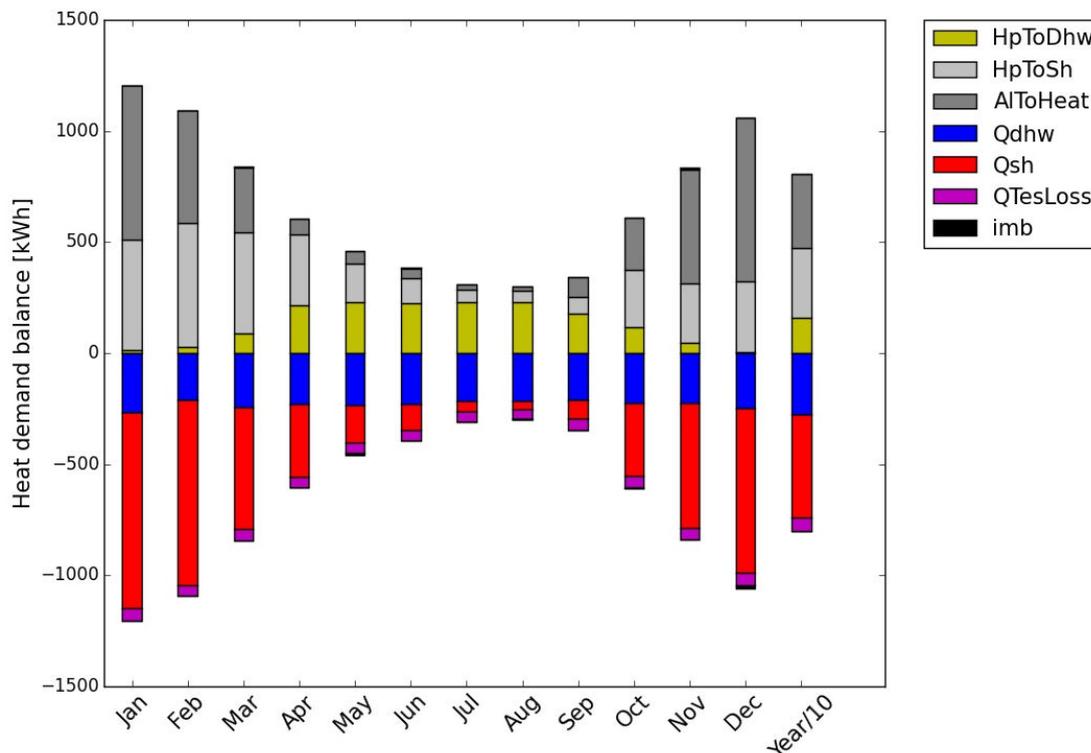


Figure 6: Monthly and yearly heat balance for the case base. The yearly value is divided by 10, Qsh in summer months are a result of hourly time steps in combination with a model that does not take into account the thermal inertia of the building.

A large part of the heating demands in winter are provided directly by the Al-to-H<sub>2</sub> converter. It has a priority to provide DHW and thus the heat pump does not need to work at high temperatures in winter, when the ambient air is a low temperature source. As soon as spring approaches, excess electricity becomes available and is used to regenerate the aluminum in the central Al-Regenerator plant from the aluminum hydroxide that was produced in winter. In spring and summer the Al-to-H<sub>2</sub> converter is seldom used, since there is enough electricity from the PV system and the heat pump is used for heating.



The electric energy balance of the system is shown in Figure 7. The energetic quantities that are shown are:

- PvToSys : electricity provided from the PV to the system
- BatToGrid : electricity provided from the battery to the grid
- GridToSys : electricity purchased from the grid
- AluToSys : electricity provided from the Al-to-H<sub>2</sub> converter
- Household : electricity demand from the household
- Hp : electricity demand from the heat pump

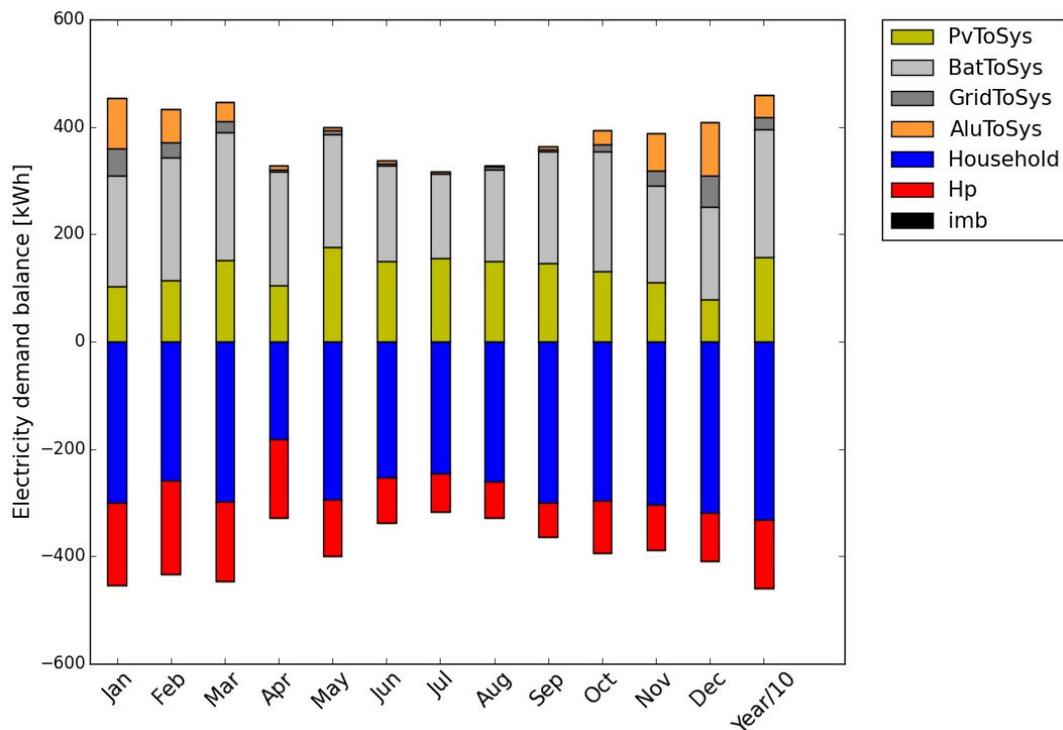


Figure 7: Monthly electric energy balance for the case base. The yearly value is divided by 10.

Around 75% of the electricity is consumed by the household (lighting and appliances), only the remaining 25% is used for the heat pump. A great part of the electricity is provided by the combination of PV and battery storage directly, without the use of the long term storage in aluminum. In winter, a small share is provided from the Al-to-H<sub>2</sub> converter and fuel cell combination. In winter, some small electricity exchange with the grid still occurs. This remaining grid-exchange is most likely due to the size of the battery and the power ratings of the components, and may be also influenced by not yet optimized control and use of storage capacities. However, increasing the battery size or power for the small amount of remaining grid-exchange does not seem to be economic or even necessary.

The monthly distribution of the PV production is shown in Figure 8. The energy provided to the household and heat pump as well as the electricity provided to the battery are relatively constant during the year. The annual variability of the PV



production that leads to excess electricity at local level is used to regenerate the aluminum in the central plant.

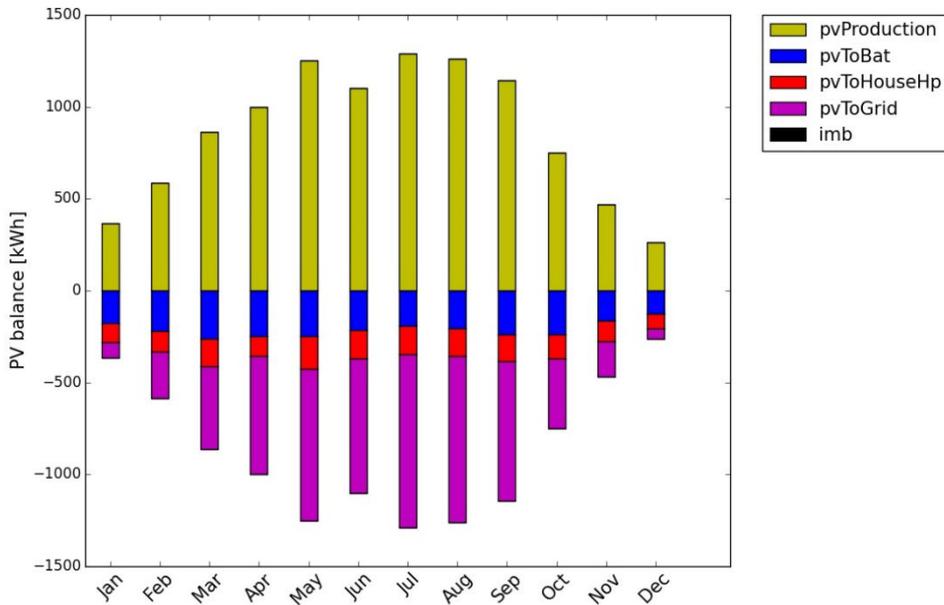


Figure 8: Monthly electricity balance of the PV production.

#### 4.4 Cost calculations

For each system the annuity costs are calculated following the methodology of VDI 2607 (2012). The main assumptions for the economic analysis are given in Table 9. With the envisaged system, energy is still transmitted through the grid from the site of PV production to the aluminum smelter, and to a lesser extent also to even out short term – but not seasonal – mismatches of electricity production and consumption. The variable cost of this electricity transmission services of the grid operator as well as other parameters of the cost calculation are listed in Table 9.

Table 9: Assumption for the calculation of the energy generation cost.

Interest rate	1% per year
Maintenance	1.0% of investment cost per year
Electricity transmission	0.06 CHF/kWh

The estimated present and future cost of key technologies and components involved in the proposed concept for a single family house are shown in Table 10.

Fuel cells for electricity supply of buildings have entered the market not so long ago and are estimated to cost 10'000 CHF/kW<sub>el</sub> today. Cost savings are possible because the usual methane to H<sub>2</sub> reformer can be spared, but these savings have



not yet been considered in this calculation. Considering this, the future decrease of price is expected to be large, in the range of 50% or more.

Current cost of PV are assumed to be 3'000 + 1'550 CHF/kW<sub>p</sub>. Future cost of PV are based on the study of the EU PV Platform<sup>9</sup>, which foresees a cost of 900 €/kW<sub>p</sub> for 5 kW<sub>p</sub>, about 700 €/kW<sub>p</sub> for 50 kW<sub>p</sub> and 530 €/kW<sub>p</sub> for 1 MW<sub>p</sub> in 2030. From these values we assume a future cost of PV of 1'500 + 750 CHF/kW<sub>p</sub>.

*Table 10: Assumptions for today's and future cost considering installation in a single family house.*

<b>Device</b>	<b>Cost today</b>	<b>prospective cost</b>
	<b>[CHF]</b>	<b>[CHF]</b>
Fuel cell	10'000/kW <sub>el+th</sub>	5'000/kW <sub>el+th</sub>
PV	3'000+ 1'550/kW <sub>p</sub>	1'500+ 750/kW <sub>p</sub>
Battery	3'000+ 1'550/kWh	500+ 250/kWh
Heat pump (including hydraulics)	15'000/unit	12'000/unit
Thermal energy storage	2'000/m <sup>3</sup>	1'200/m <sup>3</sup>
Al-to-H <sub>2</sub> converter	5'000/unit	5'000/unit
Aluminum	2/kg	2/kg

The cost of small home battery units is today in the range of 2'000 CHF/kWh capacity. However, in the automotive industry Li-ion-battery packs sell for around 500 – 600 CHF/kWh, and cost is assumed to be reduced to 200 CHF/kWh in 2025<sup>10</sup>. We assume a cost for today of 3'000 CHF + 1'550 CHF/kWh, and a possible future cost of 500 CHF + 250 CHF/kWh.

Today, the cost of a small heat pump unit, including installation, is in the range of CHF 15'000. Given the maturity of the technology, only a small cost reduction can be assumed for the future. Thus, our projected cost for the future is around CHF 12'000.

The cost of a simple thermal energy storage (TES) is today around 2'000 CHF/m<sup>3</sup>. A possible cost reduction to around 1'200 CHF/m<sup>3</sup> is assumed.

Today's and future cost of the Al-to-H<sub>2</sub> converter are unknown, since no prototype has been built yet. However, the Al-to-H<sub>2</sub> converter is involving a single unidirectional chemical reaction (not bidirectional like batteries), that corresponds to a corrosion process that occurs naturally after activation of the passive surface of the aluminum. Thus, a relatively low cost of 5'000 CHF per unit has been assumed. The same cost is assumed for the future.

Finally, we have assumed a price of 2'000 CHF per ton of aluminum for our seasonal storage "solar" fuel, corresponding to the world market price of aluminum today. This is a strong simplification for several reasons. First of all, about 25% of the world market price is the price of the invested electric energy. Since this energy will be covered by PV in our system, the cost of this energy has already been accounted for in the investment and maintenance cost of the PV system. Furthermore, the total production cost of aluminum for the world market includes

<sup>9</sup> Vartiainen, E., Masson, G. & Breyer, C., 2015. PV LCOE in Europe 2014-2030 - Final Report. European PV Technology Platform Steering Committee - PV LCOE Working Group.

<sup>10</sup> <https://www.mckinsey.com/business-functions/sustainability-and-resource-productivity/our-insights/battery-technology-charges-ahead>



cost for bauxite mining and digestion, which we would not have to account for in our process. On the other hand, part of the world market aluminum is recycled aluminum that is likely to be produced with lower cost than aluminum from bauxite ore. As a conclusion, the actual fuel price that would include the collection of aluminum hydroxide and transport to a factory, calcination and smelting process based on inert electrodes, shaping into the final product for the Al-to-H<sub>2</sub> converter, and transport to the site of use, remains difficult to estimate.

#### 4.4.1 Cost calculation for a single family home

The cost calculation for the base efficiency scenario and today's cost are shown in Table 11. For a single family house, an energy cost of 0.5 CHF/kWh can be achieved with today's estimated market prices for all components.

Table 11: Investment cost and energy generation cost for the base scenario and cost of today.

Major Component	Costs [CHF]	Size	Life time [years]	Total Costs [CHF]	
PV	3000+ 1550/kWp	9.6 kWp	25	17'880	(28%)
Battery	3000+ 1550/kWh	10 kWh	15	18'500	(29%)
Thermal Storage	2000/m <sup>3</sup>	1.0 m <sup>3</sup>	40	2'000	(3%)
Heat pump	15'000/unit	4 kW	25	15'000	(23%)
Fuel Cell	10'000/kW <sub>el+th</sub>	0.6 kW <sub>el+th</sub>	20	6'000	(9%)
Al-to-H <sub>2</sub> converter	5'000/unit	0.25 kg/h	25	5'000	(8%)
	<b>Total Investment Cost</b>			<b>64'380</b>	
Annuity	Total costs over lifetime			5506/a	
	Share of Investment			3448/a	(63%)
	Share of Al "solar fuel" (2 CHF/kg)			516 kg	1032/a (19%)
	Share of Maintenance (1% investment cost)			644/a	(12%)
	Share of Transmission grid (0.06 CHF/kWh)			6430 kWh	386/a (7%)
Share of Feed-in Al (-0.2 CHF/kWh)			18 kWh	-4/a (0%)	
<b>Energy generation cost (annuity)</b>			<b>0.51</b>	<b>CHF/ kWh</b>	

A cost sensitivity analyses was carried out for the price of each device, starting from the base efficiency and today's cost. As shown in Figure 9, cost-change of aluminum "solar fuel", PV, heat pump and battery have a high influence on the total cost. The cost of the Al-to-H<sub>2</sub> converter and fuel cell are also significant. However, the changes in cost of thermal storage are far less important for the cost-levels that were assumed.

Table 12 shows a cost projection for the system into the future, still assuming a base efficiency scenario. As can be seen, a combined electricity and heat generation cost of around CHF 0.31/kWh may possibly be achieved in a single family house with the envisaged system. From these results it can be seen that cost of the aluminum material used every year is an important factor with a contribution of 31% on the annuity cost. Hence a better estimation of the cost of this process will help to improve the forecast. The investment cost has a share on the annuity of 48%.

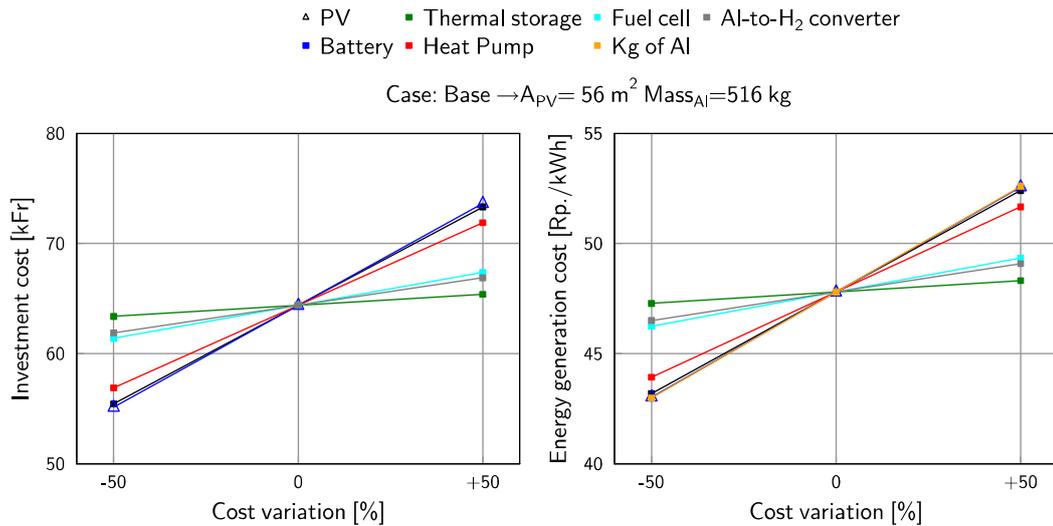


Figure 9: Cost variations of the system components for the scenario base efficiency and present cost.

Table 12: Investment cost and energy generation cost for the base scenario and projected future cost.

Major Component	Costs [CHF]	Size	Life time [years]	Total Costs [CHF]	
PV	1500+ 750/kWp	9.6 kWp	25	8'700	(26%)
Battery	500+ 250/kWh	10.0 kWh	15	3'000	(9%)
Thermal Storage	1200/m <sup>3</sup>	1.0 m <sup>3</sup>	40	1'200	(4%)
Heat pump	12'000/unit	4 kW	25	12'000	(36%)
Fuel Cell	5'000/kW <sub>el+th</sub>	0.6 kW <sub>el+th</sub>	20	3'000	(9%)
Al-to-H <sub>2</sub> converter	5'000/unit	0.25 kg/h	25	5'000	(15%)
	<b>Total Investment Cost</b>			<b>32'900</b>	
Annuity	Total costs over lifetime			3329/a	
	Share of Investment			1586/a (48%)	
	Share of Al "solar fuel" (2 CHF/kg)			516 kg	1032/a (31%)
	Share of Maintenance (1% investment cost)			329/a (10%)	
	Share of Transmission grid (0.05 CHF/kWh)			6430 kWh	386/a (12%)
	Share of Feed-in Al (-0.2 CHF/kWh)			18 kWh	-4/a (0%)
<b>Energy generation cost (annuity)</b>			<b>0.31</b>	<b>CHF/ kWh</b>	

The estimated investment cost shares using today and future cost for the base case efficiency scenario are shown in Figure 10. According to this evaluation, the most relevant investment cost today are the battery and the PV system. However, with the high potential of cost reduction of these two components, the heat pump may become a dominant cost part (see Figure 12 right), followed by the PV system and the Al-to-H<sub>2</sub> converter.

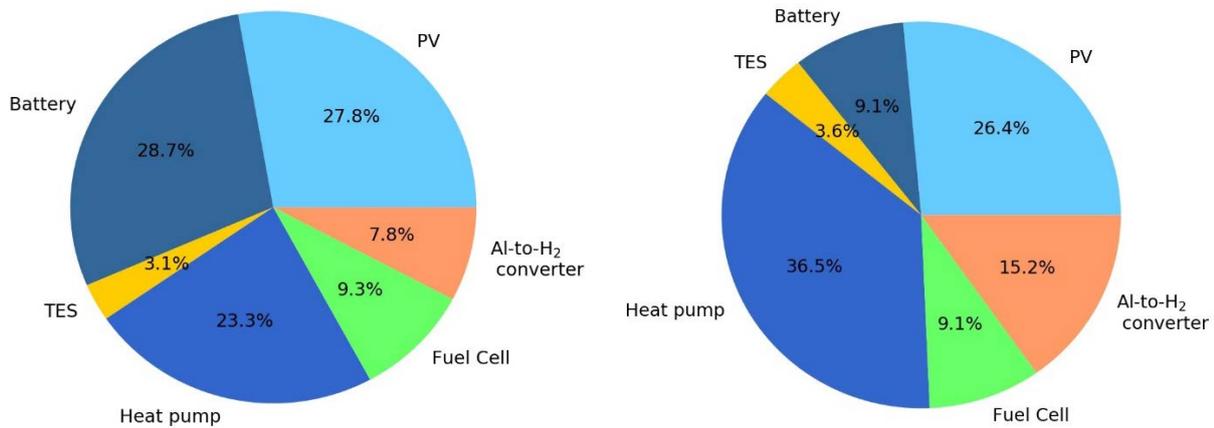


Figure 10: Investment cost shares for base case efficiency scenario with today (left) and future (right) costs.

Figure 11 shows a comparison of the cost of supplying useful heat and electricity to the building, per kWh of energy unit delivered, for three different efficiency scenarios (min, base and max) and for present as well as for future cost assumptions. Interestingly, the efficiency of the different components such as the Al-to-H<sub>2</sub> converter, the fuel cell and the smelting process do not seem to be key for the provision of low cost heat and electricity. Much more important are the investment cost of the components such as batteries and PV that have a large cost reduction potential and therefore may lead to considerable overall cost reduction.

Finally, with a high efficiency scenario, and the forecasted cost reductions in the future, the total price for the kWh useful heat and electricity delivered may be around CHF 0.31/kWh for a single family home.

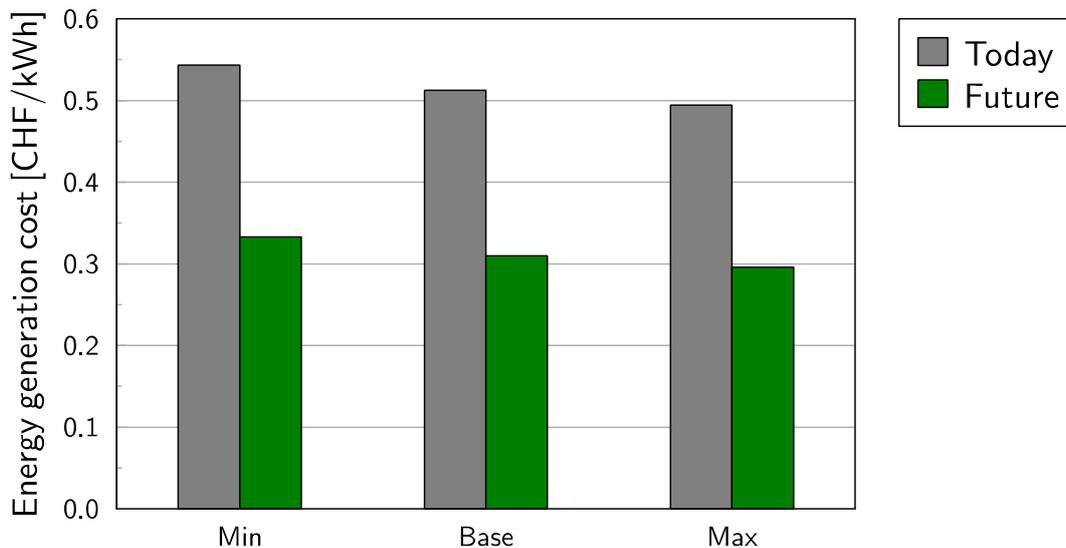


Figure 11: Energy generation cost for the three efficiency scenarios Min (left), Base (mid) and Max (right) with today's and future cost.



#### 4.4.2 Cost calculation for a multifamily building

All calculations provided until this section refer to single family homes. However, because of considerable investment cost the presented concept makes more sense for multifamily buildings (MFH). Thus, calculations and cost factors are provided in the following for a multifamily building with 8 apartments with loads as shown in Table 13.

Table 13: Specific and yearly demands for space heating, domestic hot water and electricity for a MFH with 8 apartments (960 m<sup>2</sup>).

	<b>specific demand</b>	<b>Total</b>
	<b>kWh/ m<sup>2</sup></b>	<b>MWh/ a</b>
Space heating	33	32.7
Domestic hot water	14	13.7
Household electricity	17	16.5

The sizes of main components used for the calculation of the multifamily building are provided in Table 14, and Table 15 shows the cost assumptions for the future scenario for a larger system.

Table 14: Sizes of main components used for the provisions of heating and electricity for a multifamily building.

<b>Device</b>	<b>Size</b>
Fuel cell	2 kW <sub>el+th</sub>
PV	250 m <sup>2</sup>
Battery	40 kWh
Heat pump	12 kW
Thermal energy storage	2 m <sup>3</sup>
Al-to-H <sub>2</sub> converter	4 kg/h

Table 15: Assumptions for future cost considering installation for a multifamily building.

<b>Device</b>	<b>prospective cost</b>
	<b>[CHF]</b>
Fuel cell	2'000 + 4'000/kW <sub>el+th</sub>
PV	1'280+ 640/kW <sub>p</sub>
Battery	430+ 290/kWh
Heat pump (including hydraulics)	8'000 + 500/kW
Thermal energy storage	800 + 800/m <sup>3</sup>
Al-to-H <sub>2</sub> converter	1'700+ 1'600/kW <sub>th</sub>
Aluminum	2/kg

Cost calculations for multi-family buildings are presented in Table 16 for the base efficiency scenario and projected future cost. These results show that an energy generation cost of 0.17 CHF/kWh can be expected in the future. In comparison to single family houses, the specific cost is 40% lower.



Table 16: Investment cost and energy generation cost for the base scenario and projected future cost in MFH.

Major Component	Costs [ CHF]	Size	Life time [years]	Total Costs [ CHF]	
PV	1280+ 640/kWp	42.5 kWp	25	28'480	(38%)
Battery	430+ 290/kWh	40.0 kWh	15	12'030	(16%)
Thermal Storage	800+ 800/m <sup>3</sup>	2.0 m <sup>3</sup>	40	2'400	(3%)
Heat pump	8'000+ 500/kW	12 kW	25	14'000	(19%)
Fuel Cell	2'000+ 4'000/kW <sub>el+th</sub>	2 kW <sub>el+th</sub>	20	10'000	(13%)
Al-to-H <sub>2</sub> converter	1'700+ 1'600/(kg/h)	4 kg/h	25	8'100	(11%)
<b>Total Investment Cost</b>				<b>75'010</b>	
Annuity	Total costs over lifetime			10458/a	
	Share of Investment			3792/a (36%)	
	Share of Al "solar fuel" (2 CHF/kg)			2000 kg 4000/a (38%)	
	Share of Maintenance (1% investment cost)			750/a (7%)	
	Share of Transmission grid (0.05 CHF/kWh)			32352 kWh 1941/a (19%)	
	Share of Feed-in Al (-0.2 CHF/kWh)			124 kWh -25/a (0%)	
<b>Energy generation cost (annuity)</b>			<b>0.17</b>	<b>CHF/ kWh</b>	

The overall investment cost breakdown for the multifamily building is shown in Figure 12. In comparison to a single family home, the share on the investment cost on multifamily buildings is more affected by the cost of PV (from 26% to 38%), battery (from 9% to 16%) and fuel cell (from 9% to 13%). On the other side, the investment cost is less affected by the heat pump (from 36% to 19%) and the Al-to-H<sub>2</sub> converter (from 15% to 11%).

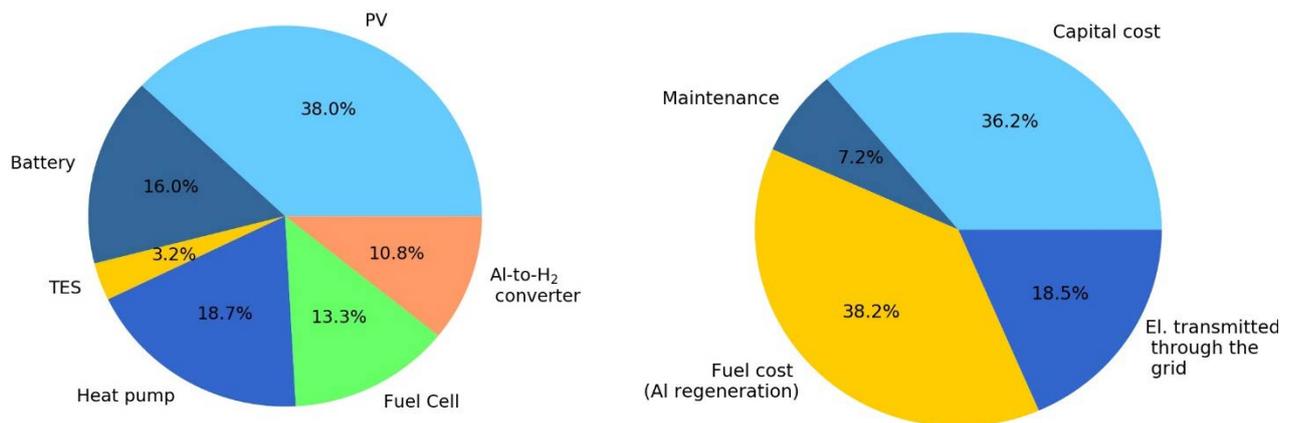


Figure 12: (left) Investment cost shares for base case efficiency scenario and future costs and (right) energy cost shares.

The overall energy cost breakdown is shown in Figure 12. The capital cost due to the investment has a share of 36%, just below the cost needed for the regeneration of the aluminium, with 38% of the total cost. The electricity transmitted through the grid accounts for 18% of the total cost. The remaining 7% will be used for maintenance.



A great part of the final energy cost is estimated to be due to the aluminum regeneration (38%). The cost of each kg of aluminum used has been assumed to be 2 CHF/kg, which is the current world market price. However, a significant part of this cost is currently due to the electricity used (25%). In our case, the price for this electricity is already accounted for in the PV system cost (generation) and in the cost for electricity transmission through the grid. Moreover, the cost of the bauxite mining and the calcination process are included in this cost, which will not be necessary in our case. Therefore, a more precise estimation of the cost for the inert electrode regeneration of the aluminum solar fuel is needed in order to obtain a better estimation of the total cost. This may decrease the overall cost of the proposed solution significantly.

#### 4.5 Life Cycle Assessment

At this early stage of novel process investigation, only a limited number of impact factors were analyzed in the LCA. These are:

- CED total: Cumulated total primary Energy Demand
- CED non-renewable: Cumulated non-renewable primary Energy Demand
- IPCC GWP100a: Global Warming Potential for 100 years

The HePoStAl “Building Electricity and Heating Unit” and PV-System (Table 17) was compared with a conventional gas boiler for heating and DHW in combination with electricity consumption from the ENTSO-E low voltage grid (Table 18). The data was extracted from SimaPro 8.3.0.0 database. For the HePoStAl system, no data is available yet for the Al-to-H<sub>2</sub> converter or for the central aluminum smelter plant, and no assumptions were taken for these.

Figure 13 shows impressively that for the conventional system only the gas and electricity consumption are relevant, for the HePoStAl system the PV system is by far the dominant factor if inert electrode technology can be used for the reduction of the aluminum. The conventional Hall-Héroult smelter process would increase the non-renewable primary energy demand by less than 20%, but it would increase the GWP by more than 75%. However, even with the conventional smelter process the PV system remains the dominant impact factor for both, the non-renewable primary energy demand as well as the GWP.

Overall, the HePoStAl system with inert electrode technology reduces non-renewable primary energy consumption by a factor of four, while it reduces GWP by more than 60%. Whereas for the conventional system the emissions are inherently connected to the purchase of natural gas and electricity from the grid, in the HePoStAl system the emissions are connected to the embodied energy in the PV system and thus reflect the share of renewable energy used for the PV production. This opens the possibility to decrease the GWP and non-renewable primary energy consumption by increasing the efficiency of PV modules or by increasing the share of renewable energies in the PV production process.



Table 17: LCA data for the assessment of the HePoStAl system.

Component	Size / Numbers	lifetime (years)	CED total (kWh oil eq)	CED non-renewable (kWh oil eq)	GWP 100a (kg CO <sub>2</sub> eq)
Air-water heat pump	4 kW	25	57	53	43
PV system	10 kWp	25	4352	3756	1091
Li-ion battery	10 kWh	25	359	322	89
Fuel cell	1 kWel	25	202	184	57
TES	2 x 600 l	25	246	212	64
<b>Total</b>			<b>5217</b>	<b>4527</b>	<b>1344</b>

Table 18: LCA data for a conventional gas boiler and electricity from the ENTSO-E grid.

Component	Size / Numbers	lifetime (years)	CED total (kWh oil eq)	CED non-renewable (kWh oil eq)	GWP 100a (kg CO <sub>2</sub> eq)
Useful heat from gas boiler	8360	1	10144	10051	2179
Electricity*	3360	1	10625	9211	1678
TES	600 l	25	123	106	32
<b>Total</b>			<b>20892</b>	<b>19368</b>	<b>3889</b>

\* from grid ENTSO-E low voltage.

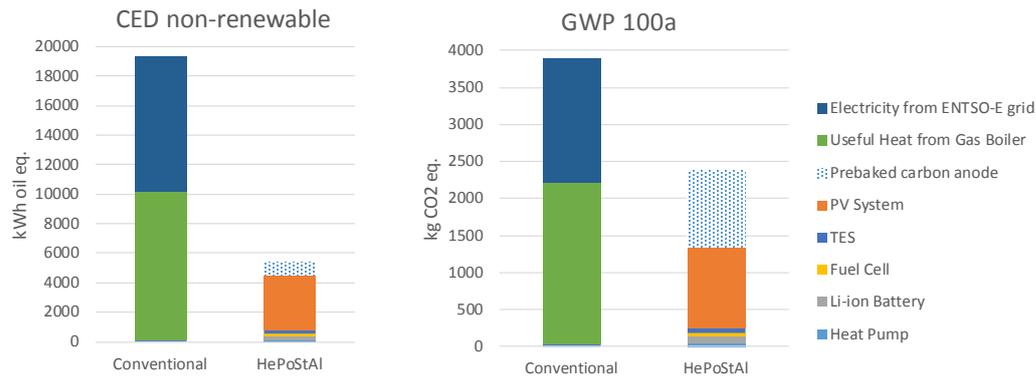


Figure 13: Cumulated primary energy (CED) non-renewable and global warming potential (GWP 100a) for a conventional gas boiler and grid electricity system and for the HePoStAl system. The impact of the carbon electrode consumption of the conventional Hall-Héroult process is shown light texturized since it is not envisaged to be part of the system.



## 5 Discussion and Outlook

The literature study has shown that with the exception of the aluminum storage cycle all components that are needed for the system (PV system, heat pump, fuel cell, home battery, thermal energy storage) are already market available products and at a high technological level. Highest cost decrease can be expected for the younger technologies that still show a dynamic price reduction in the market, such as PV system, fuel cells and home batteries.

For the aluminum storage cycle, there is a number of literature and patent claims from which it can be concluded that the necessary reactions have been demonstrated at lab-scale. These reactions are the hydrolysis of aluminum that produces hydrogen, as well as the calcination and reduction of aluminum hydroxide to the neutral form of aluminum using inert anode technology.

Estimations based on the hourly heat and electricity load of a single family home show that roughly 500 kg of aluminum are needed for the seasonal storage, corresponding to 4'000 kWh heat and electricity or roughly 40% of the combined heat and electricity demand.

The LCA study was reduced to non-renewable primary energy consumption (CED-NR) and global warming potential (GWP). The PV electricity generation system showed to be the dominant factor for the LCA of the overall system for both impact indicators. Even for the case of using the conventional Hall-Héroult process for the aluminum smelter that leads to CO<sub>2</sub> emissions from the oxidation of the carbon anodes, these emissions – surprisingly - did not outnumber the impact of the PV system. However, these emissions increase the overall GWP by almost a factor of two. From this it can be concluded that a process for the reduction of aluminum with inert anode technology is not a pre-requisite, but certainly of great benefit for the overall environmental balance of this energy storage cycle. With the Hall-Héroult smelting the CED-NR and GWP are 70% and 40% lower than for a conventional system consisting of natural gas heating and electricity from the ENTSO-E grid, and with the inert electrode technology the corresponding impact reductions are 75% and 65%.

In this integrated hybrid heat and electricity production system, it is difficult, if not impossible, to separate the cost for producing heat from the cost for producing electricity. Therefore, the cost for the generation of useful heat and electricity is evaluated as a combined cost per kWh heat and/or electricity. It is difficult to estimate the cost for the processes of inert anode aluminum smelting and for aluminum hydrolysis that both only exist at lab scale today. With the assumption of today's cost for the various market ready components, today's cost of aluminum on the world market, and a reasonable cost for the hydrolyser, as well as medium efficiency for the energy converting technologies, a price of around CHF 0.50/kWh may be expected for delivering heat and electricity to a low energy single family home with today's price assumptions, and a price smaller than CHF 0.31/kWh may result if cost reductions are happening as forecasted above all for the home battery, the fuel cell, and the PV energy generation. For the case of a multifamily building, total cost below 0.20 CHF/kWh for the delivered heat and electricity may be achieved. Interestingly, the price of the aluminum hydrolyser was not a dominating factor in the overall cost of the heat and electricity produced. However, it has to be mentioned that the assumed price for this device has a high



uncertainty, since there is no current market price and not even a full-scale prototype available for this component.

Finally, from this feasibility study it can be concluded that seasonal energy storage in aluminum may be a promising, if not revolutionary, technology for the energy turnaround:

- A 100% solar driven residential heating and electricity system that is capable of storing excess solar energy from summer to winter can be realized
- A volumetric seasonal energy storage density that is higher than the one of heating oil can be realized, leading to a required seasonal storage volume below 1 m<sup>3</sup> for a single family home.
- Both, non-renewable primary energy consumption as well as GWP are much lower than for a conventional system, and can be lowered even further with the introduction of the inert anode technology for aluminum smelter processes.
- The current (CHF 0.50/kWh) estimated price for the provision of useful heat and electricity at building level for a high energy efficiency single family home is higher than for a fossil fuel reference system at present. However, future price estimation of CHF 0.31/kWh for single family homes and of 0.17 CHF/kWh for multifamily buildings are promising, considering that this price includes all capital and operating cost of the system, electricity transmission through the grid, and the solar fuel regeneration off-site.



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## Annex A: Thermodynamic properties

### Symbols

- $\Delta H_{f,298}^{\circ}$  Standard molar enthalpy (heat) of formation at 298.15 K in kJ/mol
- $S_{298}^{\circ}$  Standard molar entropy at 298.15 K in J/mol K
- $\Delta G_{f,298}^{\circ}$  Standard molar Gibbs energy of formation at 298.15 K in kJ/mol
- $C_{p,298}^{\circ}$  Molar heat capacity at constant pressure at 298.15 K in J/mol K
- $C_p^{\circ}$  Heat capacity [J/(mol·K)] at temperature T, in temperature range indicated in the table and expressed by the equation:  $C_p^{\circ} = a + bT + c'/T^2$

### Thermodynamic data

From standard enthalpy of formation ( $\Delta H_{f,298}^{\circ}$ ) presented in Table 19, the enthalpy of reaction is calculated using Eq. 11

$$\Delta H_{\text{reaction},298}^{\circ} = (\sum n_p \Delta H_{f,298}^{\circ})_{\text{products}} - (\sum n_r \Delta H_{f,298}^{\circ})_{\text{reactants}} \quad \text{Eq. 11}$$

Table 19: Standard thermodynamic data at 298.15 K for the species involved in the presented reactions.

Symbol	$\Delta H_{f,298}^{\circ}$ (kJ/mol)	$S_{298}^{\circ}$ J/(mol·K)	$\Delta G_{f,298}^{\circ}$ (kJ/mol)	$C_{p,298}^{\circ}$ J/(mol·K)	Coefficients of the equation $C_{p,298}^{\circ} = f(T)$			$\Delta T$ K
					a	$b \cdot 10^3$	$c' \cdot 10^{-5}$	
Al (cr)	0	28	0		20.67	12.38	0	298-933
H <sub>2</sub> (g)	0	131	0	28.8	27.28	3.26	0.50	298-3000
C <sub>graphite</sub>	0	6	0	8.53	17.15	4.27	-8.79	298-2300
O <sub>2</sub> (g)	0							
Al <sub>2</sub> O <sub>3</sub> (cr)	-1675	51	1582	79	114.6	12.89	-34.31	298-1800
H <sub>2</sub> O (l)	-286	70	-237	75.3	-	-	-	298
H <sub>2</sub> O (g)	-242	189	-229	33.6	30	10.71	0.33	298-2500
Al(OH) <sub>3</sub> (s)	-1277	85	-1150					
AlO(OH)	-1003							
CO <sub>2</sub> (g)	-394	214	-394					298-1200

### Sources

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Qiyuan, C., Wenming, Z., Songqing, G., Guanqun, Y., Huifang, Z., and Zhonglin, Y. (1995). Determination of the standard molar enthalpy of formation of  $\alpha$ -AlOOH (diaspore). The Journal of Chemical Thermodynamics 27, 443–446.

## Annex B: Reaction mechanism

The reaction mechanism of aluminum with water was investigated both for hydrogen production applications and for inhibiting the reaction between the aluminum particles and water. The destruction of the native alumina layer ( $\text{Al}_2\text{O}_3$ ) is the main part.

The following reaction mechanism between aluminum powder and water from humid air was proposed by Wang et al. 2017b; Wang et al. 2017c:

- Hydration of the protective oxide film and reaction between the dense and protective alumina layer ( $\text{Al}_2\text{O}_3$ ) from the surface and water (Eq. 12, Figure 14).



- Hydrogen formation (Eq. 13):  $\text{Al}(\text{OH})_3$  reacts with the aluminum core and produces hydrogen. The hydrogen accumulates until the tension from the  $\text{Al}(\text{OH})_3$  film exceeds the critical value, then the film breaks and hydrogen is released. The aluminum core is no longer protected and reacts directly with water according to Eq. 14.



Combining the equations above, the overall reaction is obtained (Eq. 14). The authors of this research have focused on avoiding the reaction above to prevent the hydrogen explosion in a wet aluminum dust collector.

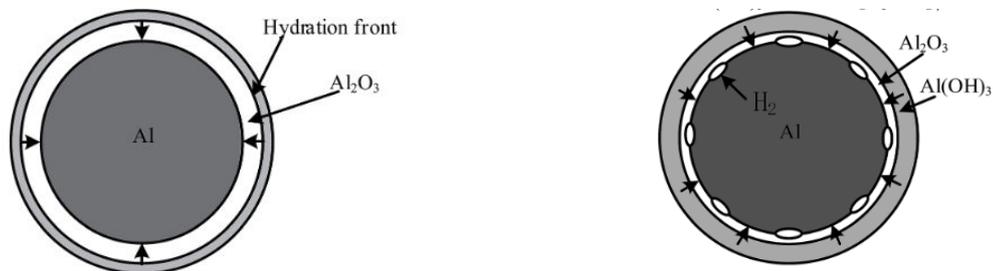


Figure 14: Hydration of the protective oxide film from the surfaces of the aluminum particles (left) and hydrogen production from the reaction of aluminum and water (right); source: Wang et al. 2017b.

A similar mechanism (Figure 15) for the destruction of the native oxide layer was proposed by Kanehira et al. 2013 for the case of hydrogen formation from aluminum powder corrosion in calcium hydroxide solutions. In this case, the aim was to promote the reaction between aluminum and water to produce hydrogen as an energy source. In a first step, the reaction of protective alumina and water leads to the modification of the Al-O-Al bonds to Al-OH (Eq. 15) and formation of oxide hydroxide ( $\text{AlOOH}$ ). This reacts with water (Eq. 16) to form aluminum hydroxide -  $\text{Al}(\text{OH})_3$ . The  $\text{Al}(\text{OH})_3$  further reacts and calcium based products (katoite) and hydrogen are obtained.



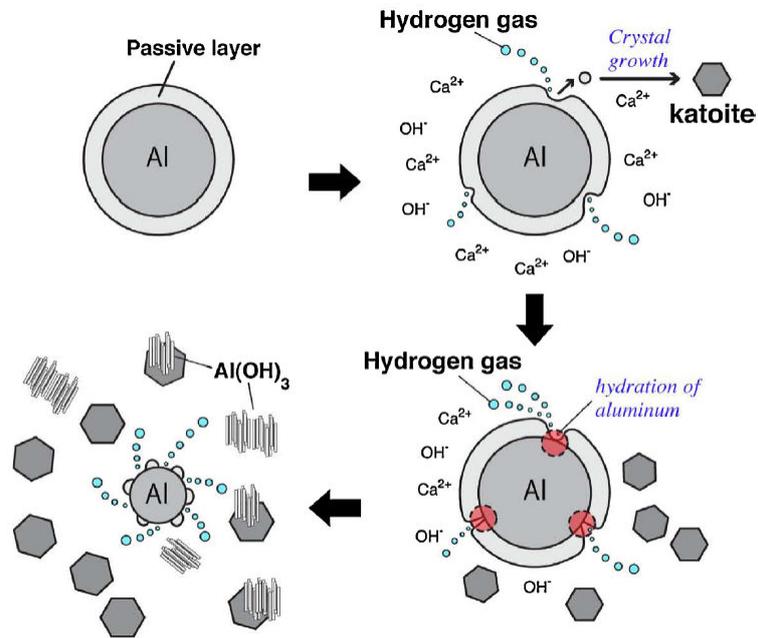


Figure 15: Aluminum corrosion in aqueous solution of calcium hydroxide  $\text{Ca}(\text{OH})_2$ ; source: Kanehira et al. 2013.