

# Energy Systems: the Importance of Energy Storage

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Energy storage is considered the key element in an energy system that organizes production, consumption and transport of electricity in a smart way. Already today a multitude of energy storage technologies is at our disposal. They scale from large pumped-storage power plants to small battery systems with high energy and power density. This article tackles the question whether we need a novel architecture of the energy system and how energy storage technologies enable the design of self-sustaining, largely autonomous energy clusters.

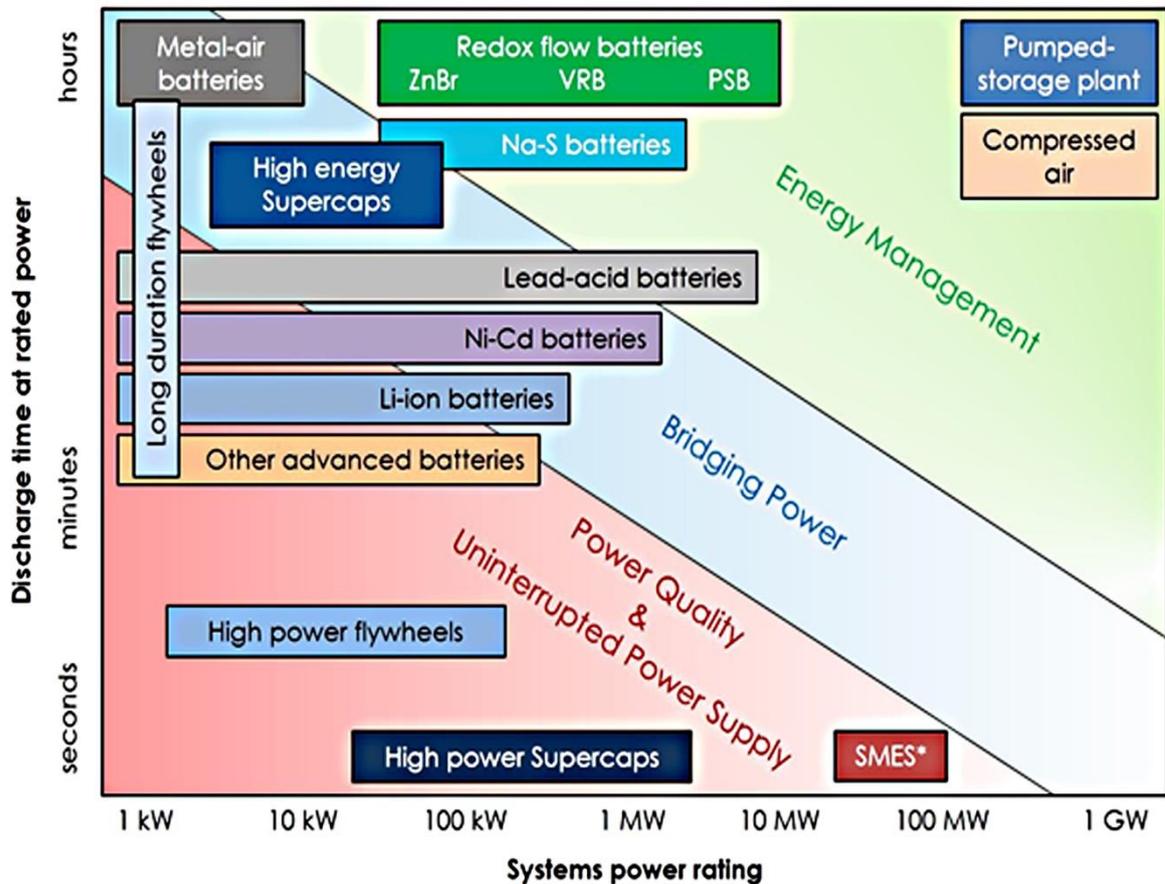
## 1. Introduction

The German term ‘Energiewende’ became a synonym for the transformation of the German energy system. It refers to the move towards an energy supply generated primarily from renewables by 2050 [1]. This requires the energy system to be fundamentally restructured, from a centralized (one producer \* many consumers) to possibly a decentralized operation (many producers \* many consumers). Amongst others, the transformation of the energy system implies two major challenges: (i) A technological challenge to develop efficient energy storage technologies that can compensate the volatile generation from renewable energy sources and (ii) a conceptual challenge to design novel architectures of the energy system, which enables the self-sustainability of individual energy clusters and sets the goals for hardware development.

## 2. The challenge: different forms of energy and how to store them

The technical performance of energy storage devices is mainly described by four key parameters. The energy density (i) is the amount of energy stored in a system of given mass (gravimetric) or a region of space (volumetric), while the power of an energy storage device per mass or volume is referred to as the power density (ii). The time of energy storage characteristic for a specific device design is called storage time (iii) and internal reactions, which reduce the stored charge in a device without any load connected in the external circuit is the so-called self-discharge (iv).

The above-described criteria apply to different technical realizations of energy storage systems. One generally distinguishes between thermodynamic energy storage devices that store energy as latent heat, and electrical energy storage devices, which allow multiple ways of energy conversion. A representative of the first category is building material featuring micro-encapsulated phase change materials (PCMs) that absorb heat when they change from solid to liquid and release heat vice versa [2]. The second category is represented by (super-) capacitors (energy stored in electromagnetic fields), batteries (energy stored in the charge state of single molecules within an encased system) or flywheels and pumped-storage power plants (energy stored mechanically). Furthermore, chemicals (such as hydrogen) can be used for long-term energy storage in combination with converters (e.g. fuel cells).



\*) SMES: Superconducting magnetic energy storage

Fig. 1. Comparison of power rating and discharge time for various energy storage systems

Fig. 1 puts several battery related technologies into context with electrical and mechanical energy storage devices. In general, electrochemical energy storage possesses a number of desirable features, including pollution-free operation, high round-trip efficiency, long cycle life, low maintenance, as well as flexible power and energy characteristics to meet different grid functions (like load leveling and power quality management) [3]. Therefore, the next section focuses on the most relevant electrochemical energy storage systems.

### 3. The devices: selected energy storage systems

Electrochemical energy storage devices can be classified in terms of their diverse operating principles. Regardless of their specific internal chemistry, batteries store energy through charge transfer reactions within their electrode structure. Redox flow batteries, in contrast, possess storage tanks containing redox species that are continuously circulated through the cell under change of their charge state. In supercaps, an electrical double-layer arises at the electrode/electrolyte interface, i.e. energy is stored in the electromagnetic field between spatially separated charges. Consequently, supercaps could be categorized as both, electrochemical and pure electrical energy storage devices. Finally, fuel cells represent yet a different, non-rechargeable kind of electrochemical storage system, since the energy is stored in the reactants (hydrogen, ethanol, etc.) that are externally fed to the device.

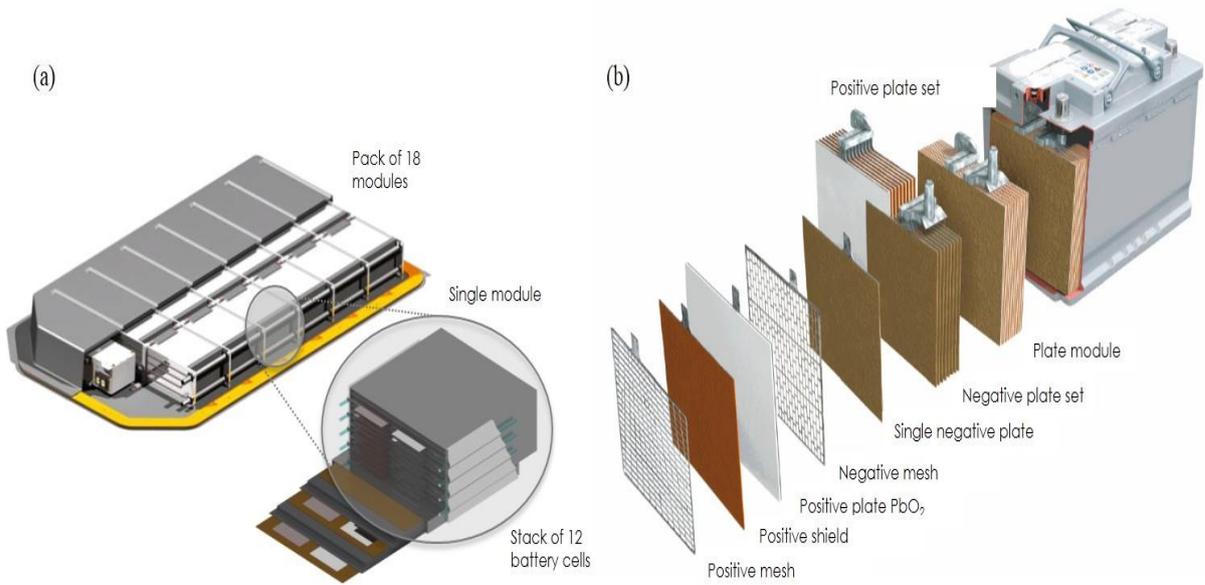
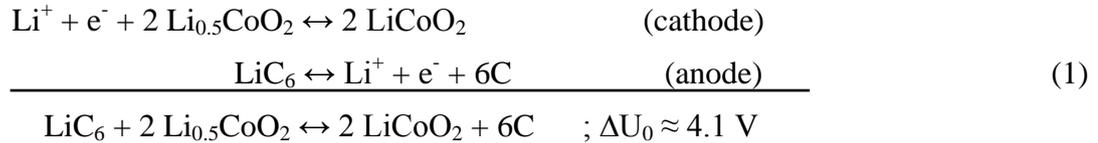


Fig. 2. (a) Li-ion battery pack comprised of 216 single cells in 18 modules [4],  
 (b) Standard lead-acid car battery.

### 3.1. Li-ion batteries

Fig. 2 compares a state-of-the-art Li-ion battery pack used in battery electric vehicles (BEVs) with a standard lead-acid car battery. The mature scientific approach of Li-ion technology to intercalate  $\text{Li}^+$  ions into host structures outperforms conventional batteries in terms of energy and power density, no matter what battery chemistry it is compared to (see Tab. 1). The reaction mechanism is summarized in Eq. 1.



In state-of-the-art rechargeable Li-ion batteries transition metal oxides serve as reversible cathode materials [5]. Lithiation of the transition metal oxides results in  $\text{LiMO}_2$  compounds (in most commercial systems  $M = \text{Co}$ ) that serve as the source of lithium in the cell. As an anode host structure that allows Li intercalation, most Li-ion battery types rely on graphite, whereas the standard electrolyte solutions are alkyl carbonate solvents.

Beyond the above-described graphite- $\text{LiCoO}_2$  system, that powers most of today's portable electronic devices, like laptops and cell phones, there is a new generation of Li-ion batteries that features novel anode and cathode materials. A compendious presentation of these advanced Li-ion battery concepts is far beyond the scope of this article and there are excellent reviews that provide a comprehensive overview of the recent developments [7]. However, one particular system shall be highlighted here, which renders Li-ion technology suitable for stationary applications, like load leveling etc.

By introducing lithium titanate  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO) as a new anode intercalation material and combining it with highly stable  $\text{LiMPO}_4$  cathodes, the resulting battery system

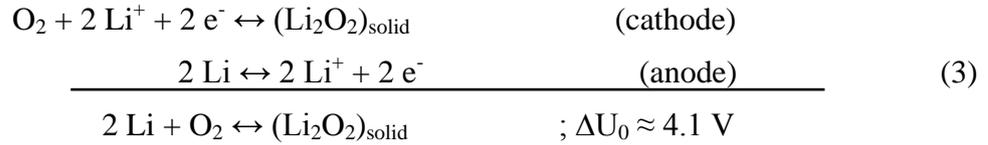
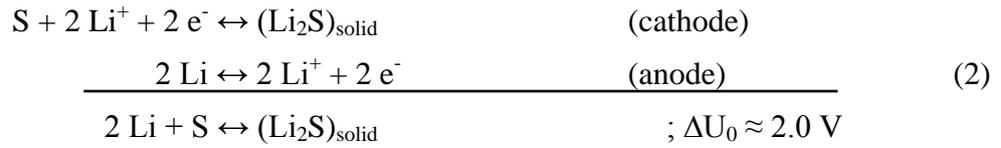
exhibits very prolonged cycle lifetime, impressive stability and excellent safety features [8][9]. LTO electrodes are inferior to graphite in terms of their capacity, which leaves LTO-based batteries with rather low energy density. However, in matters of load leveling applications for which energy density is not important, LTO electrodes seem highly suitable, because they are very fast and excel in low temperature performance [10]. At the redox potential of this electrode there are no major reduction processes of standard electrolyte solutions. Due to this fact, LTO electrodes exhibit very prolonged cycle life. As a family of cathode materials  $\text{LiMPO}_4$  and especially its representative  $\text{LiFePO}_4$  feature a practical capacity that almost reaches the theoretical one (165 out of 170 mAh/g). It furthermore possesses an excellent rate capability even at low temperatures and very good safety features. As another decisive advantage it is much less thermally active with standard electrolytes than lithiated transition metal oxides. Prototype cells employing the upper combination of novel anode and cathode materials represent impressive demonstrations of how Li-ion technology can contribute to the storage of renewable energy.

| Battery type                    | Pb  | Ni-Cd | Ni-MeH | Na-S/<br>Na-NiCl <sub>2</sub> | Li-ion    |
|---------------------------------|-----|-------|--------|-------------------------------|-----------|
| Energy density vol.<br>[Wh/L]   | 90  | 150   | 200    | 345/190                       | 300-400   |
| Energy density grav.<br>[Wh/kg] | 35  | 50    | 70     | 170/120                       | 200-300   |
| Power density vol.<br>[W/L]     | 910 | 2000  | 3000   | 270                           | 4200-5500 |
| Power density grav.<br>[W/kg]   | 430 | 700   | 1200   | 180                           | 3000-3800 |
| Self-discharge                  | +   | +     | +      | -                             | ++        |
| Fast charging                   | --  | ++    | +      | -                             | +         |

*Tab. 1. Key parameters of state-of-the-art batteries with different chemistries [6].*

### 3.2. Post Li-ion batteries

Apart from the long-commercialized Li-ion battery concept, significant research effort is put into Li-S and Li-air systems, the so-called post Li-ion batteries. For the use in BEVs the theoretical energy density of Li-ion batteries (387 Wh/kg) is too low to approach the desired driving range of ~500 km between charging [12]. The move from Li-ion to Li-S and Li-air would represent a great leap forward in terms of energy density. The reaction products on the cathode side, namely  $\text{Li}_2\text{S}$  and  $\text{Li}_2\text{O}_2$ , store more lithium and hence more charge per unit mass, than  $\text{LiCoO}_2$ . On the anode side lithium metal stores more charge per unit mass than Li-intercalated graphite electrodes. Fig. 3 depicts a schematic representation of Li-S and Li-air batteries, while Eq. 2 and 3 provide the main reaction mechanisms.



In Li-S batteries, the Li-metal anode is oxidized upon discharge, releasing  $\text{Li}^+$  into the electrolyte (vice versa upon charge). At the cathode, elemental sulfur is reduced upon discharge to form various polysulfides. These compounds then combine with  $\text{Li}^+$  to form the final discharge product  $\text{Li}_2\text{S}$  (on charging it is decomposed again to  $\text{S} + 2 \text{Li}^+ + 2 \text{e}^-$ ).

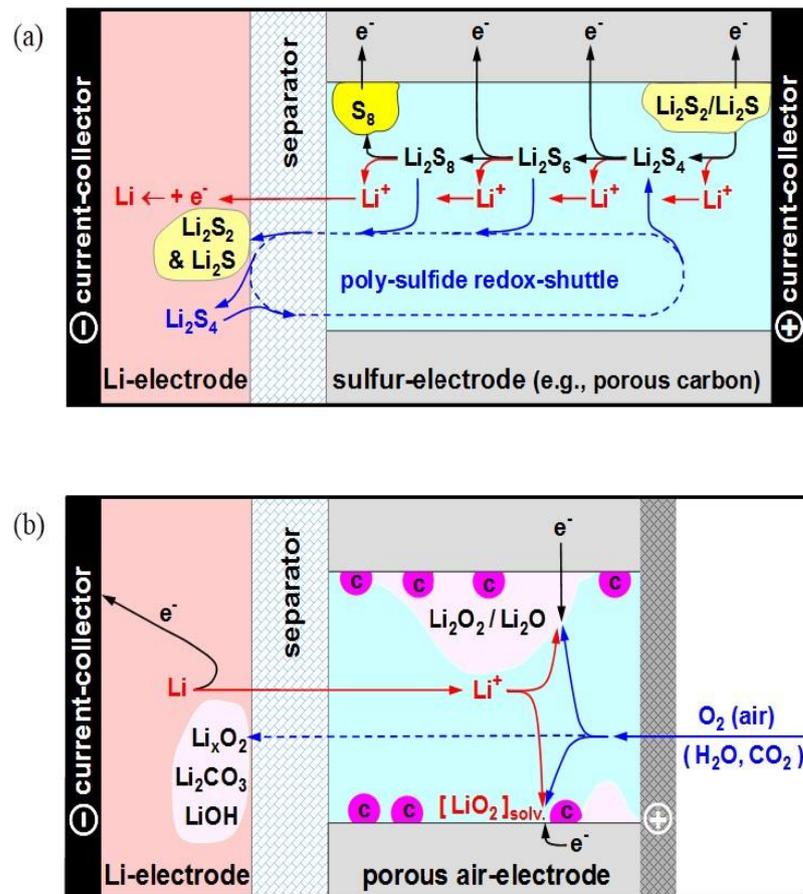


Fig. 3. Principle of Li-S (a) and Li-air battery (b) [11].

Li-S batteries represent a promising concept due to (i) the natural abundance and low cost of sulfur and (ii) the high theoretical energy density of 2567 Wh/kg [13][14]. However, major drawbacks that hampered the commercialization of Li-S technology are (i) the poor electrode rechargeability owing to the solid reaction product Li<sub>2</sub>S (“cathode clogging”) and (ii) the diffusion of polysulfide intermediates Li<sub>2</sub>S<sub>n</sub> ( $3 \leq n \leq 6$ ) to the anode (“capacity fading”).

In Li-air batteries, molecular oxygen O<sub>2</sub> from air enters the cathode’s porous carbon structure. It dissolves in the electrolyte found inside the pores and is reduced to O<sub>2</sub><sup>2-</sup> upon discharge. In combination with Li<sup>+</sup>, produced at the anode like in Li-S batteries, the final discharge product lithium peroxide Li<sub>2</sub>O<sub>2</sub> is formed (on charging it is decomposed again to O<sub>2</sub> + 2 Li<sup>+</sup> + 2 e<sup>-</sup>).

Li-air batteries offer an even higher theoretical energy density than Li-S of 3505 Wh/kg. Among others, the most apparent problem of Li-air batteries, which they also share with polymer electrolyte membrane (PEM) fuel cells, is the oxygen reduction reaction (ORR). Up to now, no research group succeeded in the synthesis of a suitable ORR catalyst to replace the high cost noble metal catalysts like Pt, Au or Pd. The designing and preparation of highly active non-noble metal cathode catalysts for Li-air batteries and PEM fuel cells is one of the most eagerly pursued targets of modern electrochemistry.

A common R&D challenge of both, Li-S and Li-air technology is the poorly controlled Li/electrolyte interface at the anode side. An improved Li-metal anode design or an alternative material is a prerequisite for both systems to advance to maturity.

### 3.3. Redox flow batteries

For energy storage in the medium scale (10 kW – 10 MW), redox flow batteries (RFBs) offer a multitude of advantages over other technologies, like flexibility (energy and power scale independently), depth of discharge, rapid response, instantaneous refueling, high cycle lifetime and good safety features (non-hazardous materials). This renders RFBs a suitable device when it comes to applications like load leveling or power quality control.

| Redox couple     | E <sub>cell</sub><br>[V] | Overall<br>efficiency<br>[%] | Energy<br>density<br>[Wh/L] | Power<br>density <sup>a</sup><br>[W/m <sup>2</sup> ] |
|------------------|--------------------------|------------------------------|-----------------------------|--|
| Iron-Chromium    | 1.2                      | 95                           | 13-15                       | 200-300  |
| All-Vanadium     | 1.6                      | 83                           | 25-35                       | 600-700  |
| Vanadium-Bromide | 1.4                      | 74                           | 35-70                       | 220-320  |
| Mega-ions        | 1.5                      | 96 <sup>b</sup>              | 250 <sup>c</sup>            | 2000   |

Tab. 2. Main parameters for the characterization of different redox flow battery chemistries (a Estimated as measured current density times cell voltage, b Coulomb efficiency of half-cell, c Estimated value based on solubility of 1 mol/L and 6 electrons per redox molecule) [16].

In typical RFBs two external reservoirs contain soluble electroactive species. Those are continuously circulated through the cell and undergo a reduction/oxidation process at the interface with the respective electrode. To maintain electroneutrality, an ion selective membrane separating the positive and the negative redox species within the two flow compartments allows the transport of non-reaction ions, e.g.  $H^+$  [15].

Successful prototypes mostly rely on the all-vanadium chemistry with a  $V^{2+}/V^{3+}$  redox couple in the negative compartment and the corresponding  $V^{4+}/V^{5+}$  redox couple in the positive compartment [17]. Tab. 2 lists several other redox flow battery chemistries and the corresponding cell voltage, efficiency, as well as energy and power density. Here, special focus shall be placed on a new concept featuring so-called mega-ions that contain multiple transition metal redox centers. Since the energy in RFBs is stored in the form of reduced and oxidized electroactive species in the electrolyte, the use of mega-ions offers a great potential. Multiple redox states and the high number of electrons per unit volume could lead to higher energy and power density than in conventional RFBs. Under electrochemical analysis, mega-ions have proven to exhibit fast and reversible multi-electron redox activity [16]. Besides, their application in RFBs also supercaps could possibly benefit from the advantageous properties of mega-ions. However, RFBs and supercaps relying on mega-ions have not reached a prototype stage yet.

#### **4. The automotive application: fueling the e-car**

Apart from energy storage for the grid the second major application of battery technology is found in sustainable personal mobility. The future of automotive propulsion is closely related to electrochemical energy storage, given fossil fuel limitations and environmental imperatives [18]. Fig. 4 proposes two concepts for fueling the e-car.

Many vehicle manufacturers rely on the state-of-the-art approach to use Li-ion batteries for the electrification of the automobile. Given an energy supply generated primarily by renewables, those battery electric vehicles (BEVs) are mainly powered by ‘green’ electricity from wind parks and solar farms. The transport and distribution of the electricity needed for charging is accomplished by the power grid and a dense infrastructure of charging stations. In order to achieve the goal of 1 million BEVs by 2020 or even a full electrification of the German car fleet (approx. 42 million BEVs) considerable efforts have to be devoted to (i) the establishment of such a charging infrastructure, (ii) the improvement of today’s Li-ion batteries [19]. For their application in BEVs, the main constraints are the relatively low energy density and the long recharge time. Without a breakthrough in the above-described next generation Li-ion/Li-S/Li-air batteries the only solution to enable comfortable long-distance driving with fully electric cars is presented by initiatives like “Better Place”, which suggest networks of fast battery switch stations [20].

In the lower part of Fig. 4 we want to highlight an innovative approach to accomplish fully electric propulsion without the need for new infrastructure. Direct ethanol fuel cells (DEFCs) convert the chemical energy carrier ethanol into electrical energy. Ethanol can be produced in a sustainable way by thermal or chemical conversion of biomass and waste. It is a liquid fuel of high energy density (8 kWh/kg, 40x higher than Li-ion batteries), non-toxic and it can be easily integrated in the existing fuel infrastructure. Thus fuel cell electric vehicles (FCEVs) powered by DEFCs represent a serious alternative to BEVs. In general DEFCs face the same R&D needs as high-temperature PEM fuel cells. The biggest challenge, however, is to achieve a total oxidation of ethanol to  $CO_2$ . An effective C-C bond scission during the ethanol oxidation is necessary to enable the utilization of all 12 electrons

in the ethanol molecule. Recent reports on the CO<sub>2</sub> current efficiencies (CCEs) present values of up to 80% [21]. In order to further enhance the reaction kinetics higher operating temperatures of 200-400°C are suggested. Consequently, this requires highly temperature resilient membranes. One potential candidate are ammonium polyphosphate composites that excel due to their good ionic conductivity and high temperature stability at up to 250°C [22]. For the interested reader, there is a comprehensive review investigating the ethanol oxidation reaction in DEFCs [23].

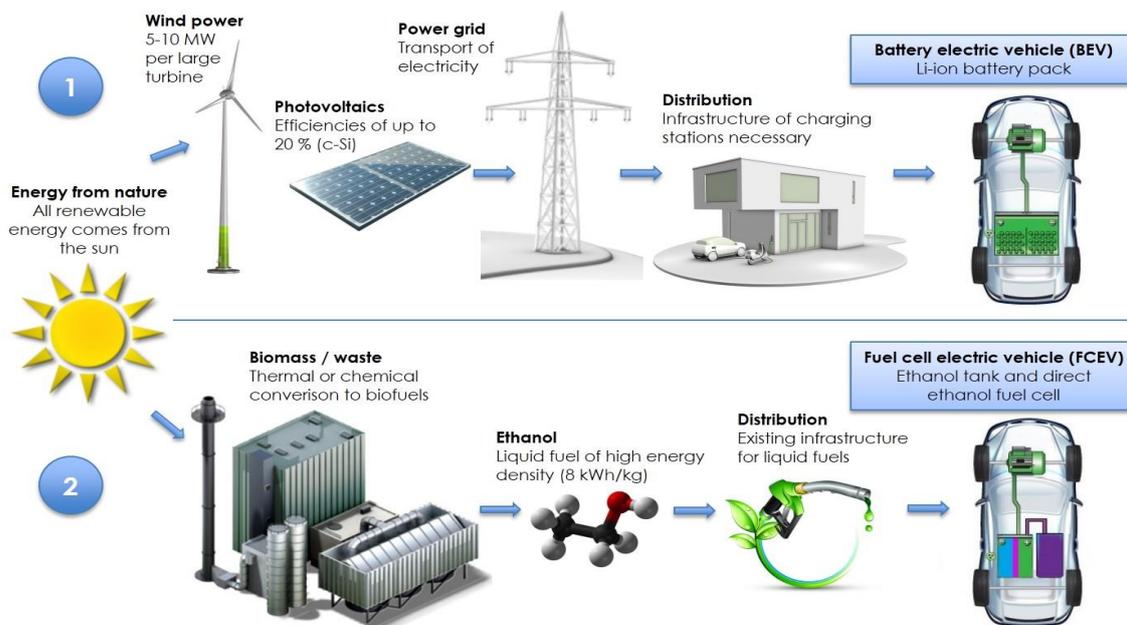
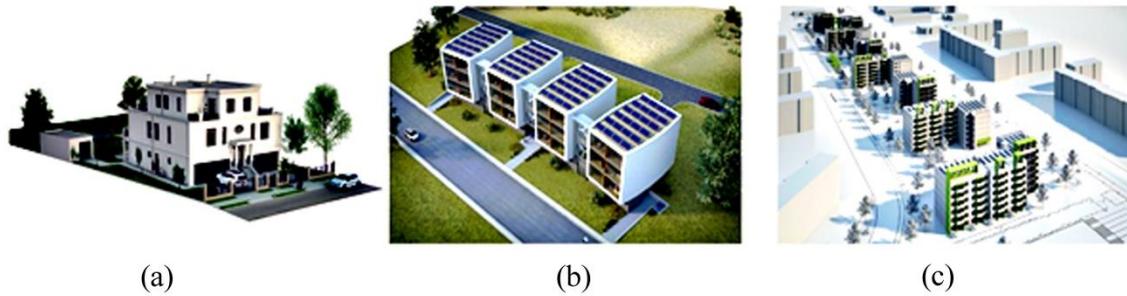


Fig. 4. Two approaches for fueling the e-car

## 5. The big picture: do we need a new energy architecture?

Coming back to the beginning of this article, a critical endeavor for researchers in the field of energy systems is to transform our energy landscape towards a sustainable and green future. Based on the existing energy storage technologies, we believe that we do not only need a restructuring and a decentralization of the electricity production, but a whole new architecture of the energy system in order to tap the full potential of a smart production, transportation and storage of electricity. As it will be evidenced later, the establishment of quasi-autonomous energy clusters can be a solution to reduce the need for grid extension considerably.

Given the rapid development of renewable energy we are currently facing, there are two design approaches one could pursue in the structuring of our energy system: The top-down approach (i) is to construct large-scale wind parks and photovoltaic (PV) sites, and to heavily invest into grid extension for the transport of electricity to the consumer and the increase of the storage capacity of the grid. This approach will most probably lead to the fulfillment or even over-fulfillment of the obligations for electricity production on the way to a completely renewable energy supply by 2050. However, in that scenario an effective energy management is restricted to a limited number of large-scale storage technologies, like pumped-storage power plants and compressed air storage sites.



*Fig. 5. Scalability of energy clusters by choice of technology from single homes (a), to blocks (b), to districts (c). Reprinted from [24].*

By contrast, the bottom-up approach (ii) is favoring self-sustaining and largely autonomous energy clusters together with a need-based, local production of electricity. By this, one could minimize the need for energy storage and greatly reduce the supplementation from the grid. With the right choice of technology for energy conversion and storage, those energy clusters could range from single-family homes, to city blocks or even whole districts, production sites and small remote villages (see Fig. 5). All of this demands the development of an efficient management structure, hereafter referred to as “computational energy science”, under which those energy clusters can act as quasi-autonomous micro grids. A novel architecture of the energy system based on energy clusters, could focus on the combination of multiple small-scale technologies (like the above-described lithium and redox flow batteries) to design generation, storage and consumption in a smart way.

Fig. 6 depicts what an energy cluster within the smart grid could look like. In an exemplary calculation, we want to outline the capabilities of those energy clusters, in terms of need-based production and autonomy.

The energy cluster we consider in the following, is a  $100 \times 100 \text{ m}^2$  five-story city block with a net floor space of  $9000 \text{ m}^2$  (see Fig. 7). The 1<sup>st</sup> floor is assumed to accommodate shops and service industry with an average electricity consumption of  $100 \text{ kWh/m}^2\text{a}$  [26]. From the 2<sup>nd</sup> to the 5<sup>th</sup> floor two-person apartments will be established. Assuming a standard size of  $80 \text{ m}^2$  per apartment, the contemplated four stories provide space for 450 apartments. Under consideration of an average electricity production of  $2500 \text{ kWh/a}$  for a two-person household the total electricity demand of the energy cluster amounts to  $2025000 \text{ kWh/a}$  [26].

On the generation side, a multitude of renewable energy converters comes into play. The roof area of  $9000 \text{ m}^2$  can be equipped with panels of advanced monocrystalline solar cells that nowadays possess an efficiency of more than 20% [27]. Presuming an irradiance of  $1000 \text{ kWh/m}^2\text{a}$ , an air mass of 1.5, a flat roof with an orientation of the panels towards the south and taking into account 25% of losses (due to shadowing, snow coverage, reflection etc.) a PV generation of  $1350000 \text{ kWh/a}$  is feasible [28]. Furthermore, organic PV covering the inner yard of the building can produce  $75000 \text{ kWh/a}$ , implying the same parameters as before and an efficiency of 10% [27]. An additional installation of eight house wind turbines with a power of 10 kW per turbine and 2000 full load hours per year could contribute  $160000 \text{ kWh/a}$ . In total, the on-site generation of the energy cluster sums up to  $1585000 \text{ kWh/a}$ .

In consequence, only a difference of  $440000 \text{ kWh/a}$  cannot be produced by the cluster itself and has to be supplemented from the power grid. This is equal to 22% of the total consumption.

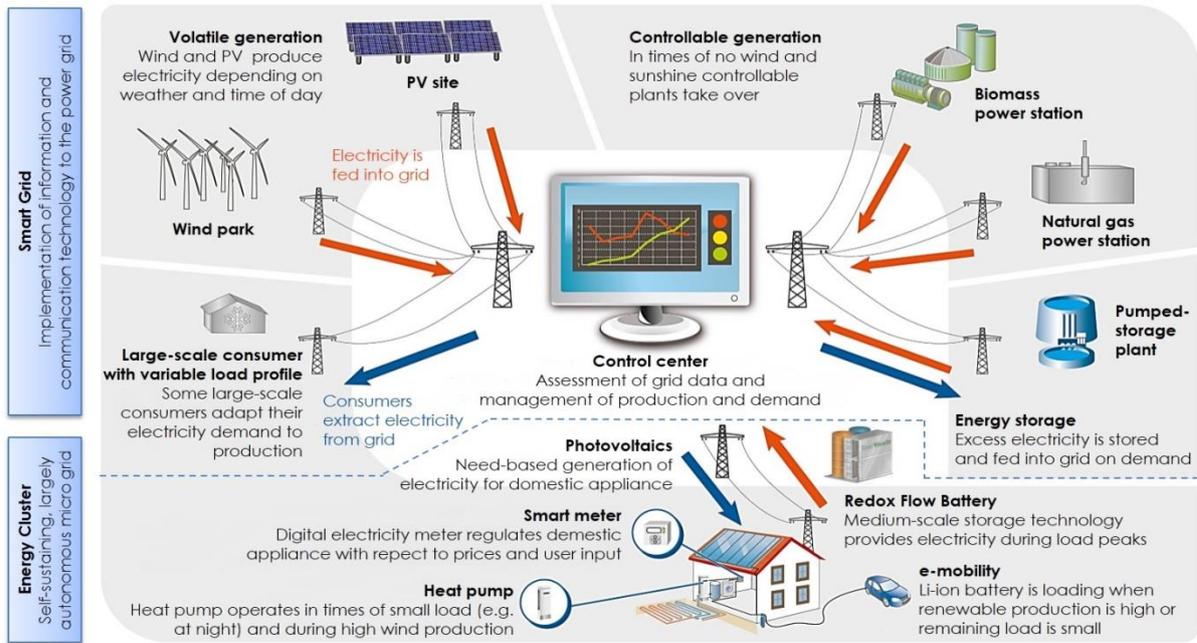


Fig. 6. Smart grid architecture featuring autonomous energy cluster. Rearranged from [25].

Besides energy demand and generation, the third pillar that the energy cluster is based on is energy storage. An ambitious goal would be to store 30% of the daily consumption, in order to account for the volatility of renewables. Upon the installation of four small-scale pumped-storage units with a volume of  $10^6$  L each, the height of 15 m from the top floor to the basement of the building results in a storage capacity of 220 kWh. An advanced redox flow battery featuring an energy density of 0.25 kWh/L would be a suitable energy storage device to store the remaining 1440 kWh. For this scale of application, the electrolyte storage tanks would need to contain 5760 L of electrolyte, which is a reasonable size for stationary devices.

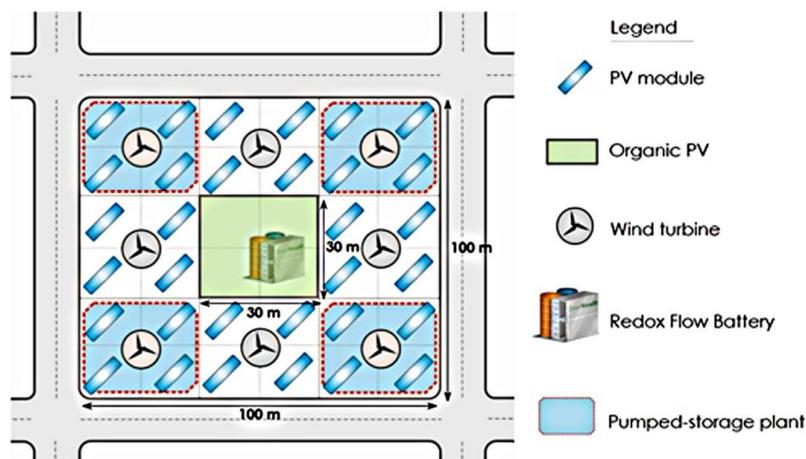


Fig. 7. Largely autonomous city block as example for energy cluster.

All in all, the results of this assessment render energy clusters a self-sustaining and largely autonomous element of a novel energy architecture.

## 6. Conclusions

The article reviewed recent developments in the improvement of state-of-the-art energy storage devices with special focus on lithium battery technology and redox flow batteries. It was shown that Li-S and Li-air batteries are potential candidates to replace today's Li-ion batteries, due to their beneficial energy and power density. New advances in active materials for RFBs render those devices prospects for stationary energy storage. All of the presented electrochemical energy storage technologies offer the potential to be a part of a novel energy architecture that relies on self-sustaining energy clusters. In an exemplary calculation it was shown that the need-based, on-site production of electricity combined with modern but existing energy storage devices can greatly reduce the supplement of electricity from the grid.

We strongly believe that the future of energy systems has to be established on the basis of "computational energy science", in which an efficient management structure sets the goals for hardware development.

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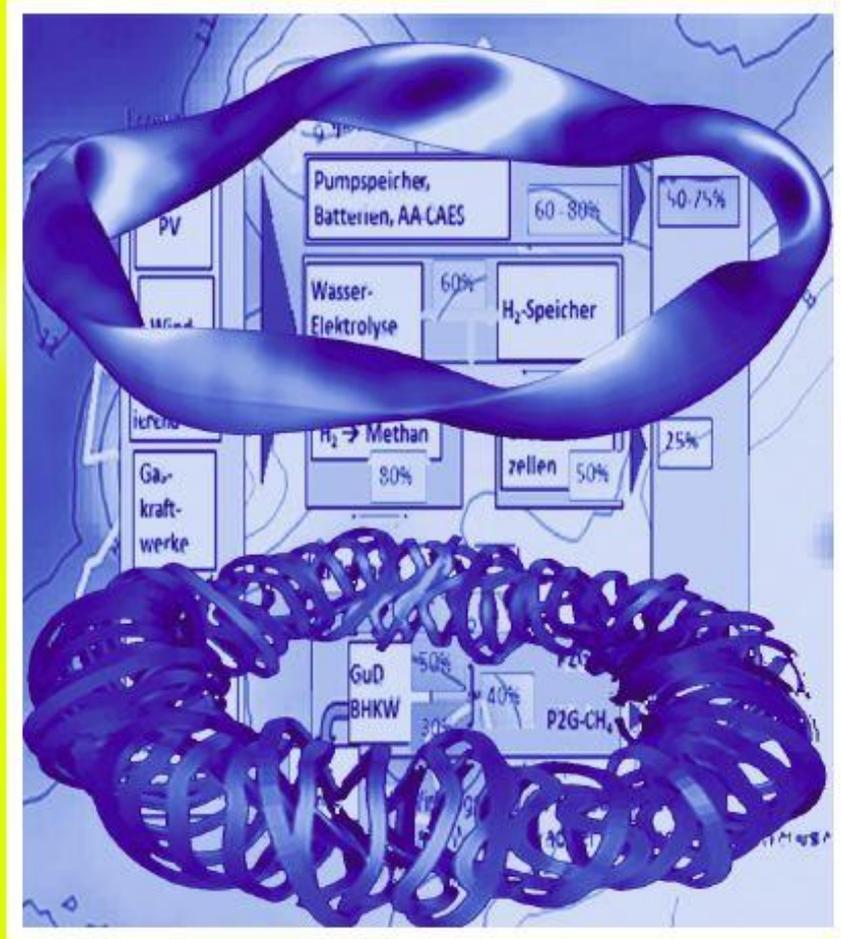
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## Technologien und Energiewirtschaft

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Haupt- und Plenarvorträge

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