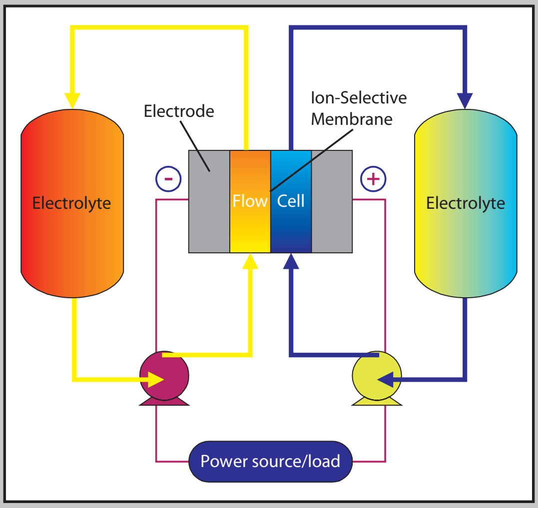
Briefing Paper

Leonardo ENERGY

Flow batteries



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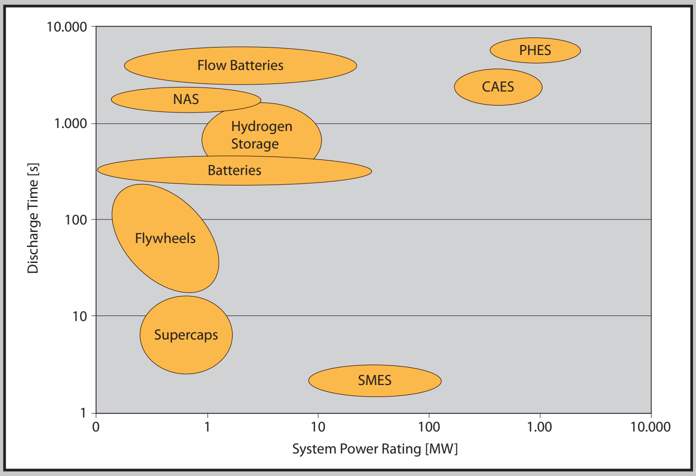

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Flow batteries

A flow battery is a type of battery that can be designed very flexibly. It can be designed for high power applications as well for high-capacity electricity storage. Other types of electricity storage, like conventional batteries or flywheels, do not show this flexibility and therefore have some limitations to their applications. Flywheels are mostly used for short durations (<5 minutes) and high power storage (> 500 kW), while batteries are used for lower power (<500 kW) and long durations (> 1 hour). Flow batteries are used for large-scale projects that require high-capacity storage and also high power storage, for instance for grid-connected electricity storage at wind farms.

In a flow battery the battery is charged and discharged by a (reversible) chemical reaction between the two liquid electrolytes of the battery. These electrolytes are not stored in the power cell of the battery as in a conventional battery, but in separated storage tanks. During operation these electrolytes are pumped through the electro-chemical reactor, in which a chemical redox reaction takes place and electricity is produced. Due to this storage of the electrolytes outside the reactor, the specifications of the battery are flexible; the power and the energy content of the system can be specified separately. It is very easy to increase the amount of electrolytes or to replace the electrolytes. Moreover, the design of the power cell can be optimized for the power rating needed, as this is independent of the amount of electrolyte used.

The development of flow batteries has reached the stage of demonstration projects. Small- scale products are already available on a commercial basis, while for the larger-scale projects demonstrations have been started. These demonstration projects prove the technology and show that it can be applied on a large scale. The costs of the technology will decrease as soon as the technology becomes available as a commercial product. Based on current feasibility studies, the life cycle costs will be lower than those of the alternatives, based on the capital costs and the expected life time. Flow batteries can be very attractive for future applications, especially for large-scale applications, like peak power support at wind farms or distribution level balancing.

Introduction

There are many technologies for storing electricity, but all have significant limitations:

- Devices for high power, like Superconducting Magnetic Energy Storage (SMES) devices or flywheels, can normally be used for a short time
- High-capacity storage systems, like batteries, generally give low power
- Solutions that are applicable to high power AND long duration, e.g. Pumped Hydro Energy Storage (PHES) or Compressed Air Energy Storage (CAES), are site-dependent and have specific requirements to the location.
- Other systems for high power and long duration have specific conditions, like sodium sulfur batteries (NaS), which have an operating temperature of about 300ºC; this is very unpractical in long-term storage situations. Moreover, upscaling of NaS systems is more expensive than upscaling of flow batteries. So these NaS batteries are especially applicable in situations in which the size of the battery is a little smaller than the typical size of flow batteries and in which the storage system cycles frequently.

Flow batteries offer a new dimension, as they can be designed for high power *as well as* long duration, while the application is not site-dependent and is also attractive in situations in which the system is not cycled frequently. The figure below shows this rough comparison of different types of electricity storage.

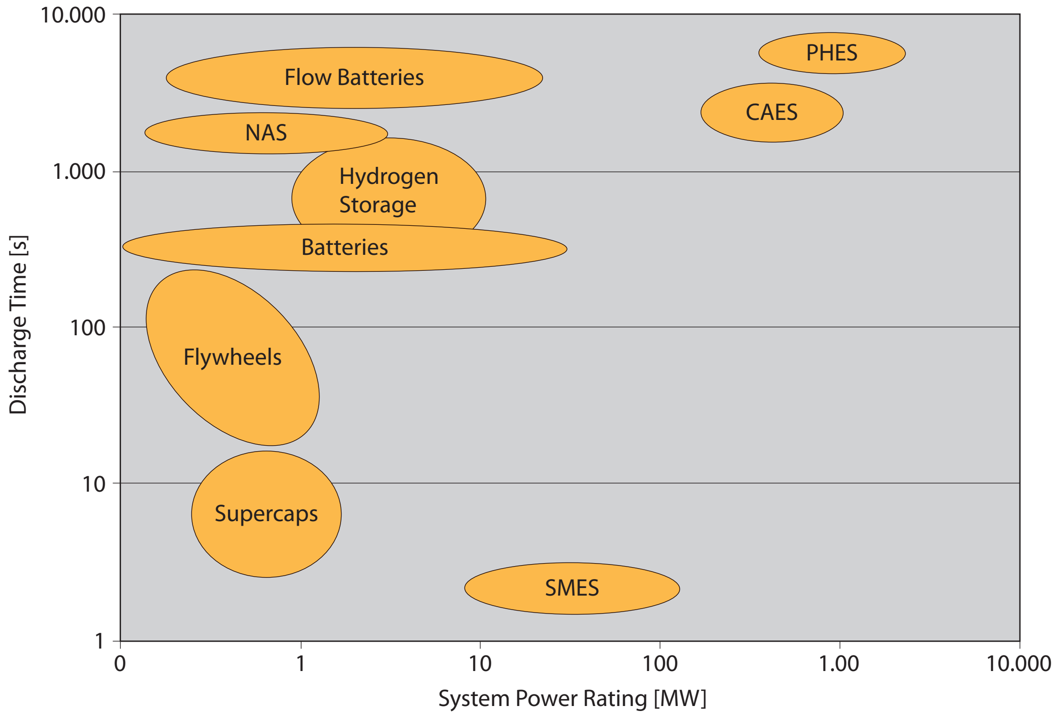

Figure 1. Comparison of different storage systems

Background

Flow batteries are a new class of batteries. These batteries are especially attractive for larger-scale applications such as utility scale. The operational principle of this flow battery differs from a conventional battery, e.g. lead acid or nickel metal hydride batteries. In the latter all components are stored in the battery; the power conversion and the electrolyte storage are combined in the battery. So in the battery the power rating as well as the energy rating are fixed, based on the type of battery used and the size of the battery.

Flow batteries work differently. In this system the power rating and energy rating are decoupled, which makes the system very flexible. In a flow battery the liquid electrolytes flow through an electrochemical cell in which chemical energy is converted into electricity. So the power rating is determined by the design of the cell stack. In this stack the reversible chemical reaction between the two electrolytes takes place. The stack determines the power of the total system. Both electrolytes are stored separately in large storage tanks outside the battery stack. The size of the tanks and the amount of electrolyte defines the energy capacity of the total storage system. The figure below shows a schematic overview of a redox flow cell.

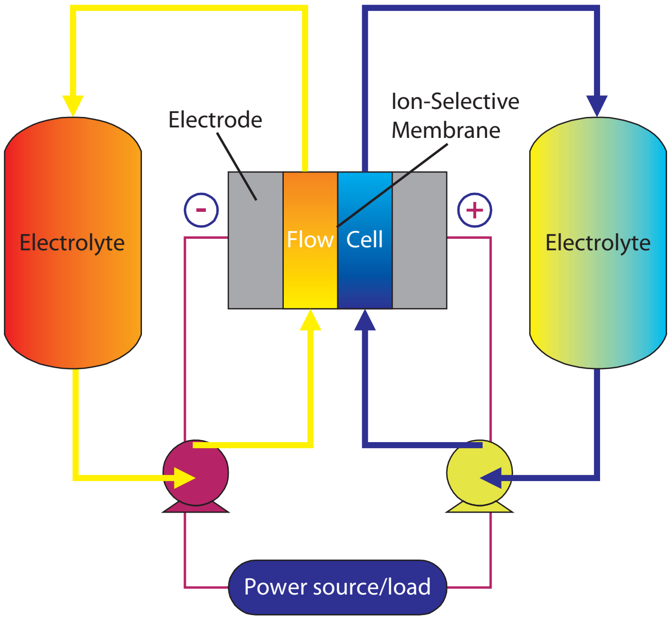

Figure 2. Schematic overview of a redox flow cell energy storage system

The costs of such a system can be divided mainly into costs of the electrochemical reactor and costs of the electrolytes with the storage tanks. If one increases the storage capacity of the system, the costs of electrolytes will increase. However, this does not affect the costs of the electrochemical reactor. Therefore, the costs per kWh to be stored or supplied by the system, will decrease.

Since the storage capacity only depends on the size of the electrolyte tanks, the flow batteries do not have any obvious scale limits. This makes it a promising technology for large-scale electricity storage.

Technologies

Flow batteries are often called redox flow batteries. The name redox flow battery is based on the redox reaction between the two electrolytes in the system. „Redox" is the abbreviation for „reduction-oxidation" reaction. These reactions include all chemical processes in which atoms have their oxidation number changed. In a redox flow cell the two electrolytes are separated by a semi-permeable membrane. This membrane permits ion flow, but prevents mixing of the liquids. Electrical contact is made through inert conductors in the liquids. As the ions flow across the membrane, an electrical current is induced in the conductors.

Theoretically, many combinations can be used as a redox couple. In practice, many combinations are not applicable, for instance because of side reactions. The table below shows the most attractive electrolyte couples proposed for use in flow batteries.

	Negative cell		Positive cell		Total cell
Couple	Electrolyte	Redox potential [V]	Electrolyte	Redox potential [V]	Standard Cell potential E_o [V]
U/U	$U^{4+} + e^- \rightarrow U^{3+}$	-0.607	$UO_2^{2+} + e^- \rightarrow UO_2^{+}$	0.06	0.7
Fe/Ti	$Ti^{3+} + e^- \rightarrow Ti^{2+}$	-0.9	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.771	1.7
Fe/Cr	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	-0.407	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.771	1.2
V/V	$V^{3+} + e^- \rightarrow V^{2+}$	-0.255	$V^{5+} + e^- \rightarrow V^{4+}$	0.991	1.2
Br/S	$S + 2e^- \rightarrow 2S^{2-}$	-0.48	$Br_2 + 2e^- \rightarrow 2Br^-$	1.087	1.5
Zn/Br	$Zn^{2+} + 2e^- \rightarrow Zn$	-0.763	$Br_2 + 2e^- \rightarrow 2Br^-$	1.087	1.9
V/O	$V^{3+} + e^- \rightarrow V^{2+}$	-0.255	$O_2 + 4H^+ + e^- \rightarrow 2H_2O$	1.229	1.5
Ti/O	$Ti^{3+} + e^- \rightarrow Ti^{2+}$	-0.9	$O_2 + 4H^+ + e^- \rightarrow 2H_2O$	1.229	2.1
Cr/O	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	-0.407	$O_2 + 4H^+ + e^- \rightarrow 2H_2O$	1.229	1.6

Table 1. Overview of most important possible electrolytes [10]

The chemical reaction determines the cell potential of the total flow battery.

Most promising redox couples

Over the past few years three types of flow batteries were developed up to the stage of commercialization and demonstration. These types are vanadium cells (V/V), Polysulphide Bromide Batteries (PSB) and zinc bromine (ZnBr). Each type has its own specifications and is developed for a specific application.

Vanadium (V/V)

Vanadium Redox Batteries (VRB) use two different vanadium electrolytes (V^{2+}/V^{3+} and V^{4+}/V^{5+}, both in a mildly acid solution). During the charge/discharge cycles, H^+ ions are exchanged between the two electrolytes through a proton-permeable polymer membrane.

The reactions during charging:

$V^{3+} + e^- \rightarrow V^{2+}$

$V^{4+} \rightarrow V^{5+} + e^-$

And during discharging:

$V^{2+} \rightarrow V^{3+} + e^-$

$V^{5+} + e^- \rightarrow V^{4+}$

As in both half cells vanadium is used, this concept eliminates the problem of cross-contamination by diffusion of ions across the membrane. The development of V/V focuses on applications in wind farms.

Polysulphide Bromide Batteries (PSB or Br/S)

In this type of flow battery solutions of sodium bromide (NaBr) and of sodium (Na) polysulphide (S_n^{2-}) are used as electrolytes. The Na^+ ions pass the membrane during charging or discharging, while Br and S are the components that emit and accept electrons. That is why it is often shortened as a Br/S system.

Reactions during charging:

$S + 2e^- \rightarrow 2S^{2-}$ ($Na_2S_4 + 2e^- + 2Na^+ \rightarrow 2Na_2S_2$)

$Br_2 + 2e^- \rightarrow 2Br^-$ ($3\ NaBr^- \rightarrow NaBr_3 + 2Na^+ + 2e^-$)

During discharging the reverse reactions take place.

PSB focuses on large-scale applications. This system has been developed by Regenesys Technologies Ltd. (and afterwards by RWE Innogy) under the name „Regenesys™". The objective was to build a grid-connected utility-scale storage system for power ratings in excess of 5 MW_e. The construction of a pilot plant of 12 MW_e/120 MWh capacity was started at the Little Barford plant. This site was used to demonstrate a completely integrated plant. However, it was never fully commissioned. In December 2003 RWE Innogy announced that it would no longer be funding this project and the development of this technology.

In 2004 VRB Power acquired an exclusive global license from RWE for all intellectual property of the PSB system. A second demonstration plant was planned in Mississippi at Tennessee Valley Authority (TVA). This site was based on the same technology as the site of RWE Innogy. However, also this plant was also canceled, as RWE didn't want to proceed with the joint venture. No new large-scale demonstration projects have been announced yet.

Zinc bromine (ZnBr)

The zinc bromine battery consists of a zinc-negative electrode and a bromine-positive electrode, separated by a micro-porous separation. Solutions of zinc and a complex bromine compound are circulated through the two compartments. This flow battery is based on another principle than the V/V and PSB systems. In a ZnBr flow battery the electrodes (Zn^- and Br^+) serve as substrates for the reaction and their performance capacity can be degraded if the battery is not completely and regularly discharged.

During charging, the zinc is electroplated at the anode and bromine is evolved at the cathode, according to the following reactions:

$Zn^{2+}\ (aq) + 2e^- \rightarrow Zn\ (s)$

$\underline{2Br^-\ (aq) \rightarrow Br_2\ (aq) + 2e^-}$

$Zn^{2+}\ (aq) + 2Br^-(aq) \rightarrow Zn\ (s) + Br_2(aq)$

And during discharging the reactions are reversed.

These batteries are mainly developed for small-scale applications. In 2004 the major developer of ZnBr systems ZBB began full-scale commercial operations with an automated manufacturing line.

<u>Characteristics flow batteries in general</u>

The main characteristics of flow batteries:

– High power: the cell potential depends on the chemical reaction used, the power rating is determined by the design and size of the power stack.
– Long duration: the energy rating depends on the amount of electrolyte used and the corresponding size of the storage tanks.
– The design of the power rating and the energy rating are decoupled.
– The system is re-fillable, electrolytes can be replaced easily.
– Most redox reactions are very rapid (fast reaction kinetics), which makes the reaction time very short. Flow batteries have a fast response and can go from charge to discharge modes in about 1/1000 s.
– The full-cycle efficiency of the battery is relatively low (75% - 80%), due to the energy needed to circulate the electrolyte and losses due to chemical reactions, e.g. forming of hydrogen.
– The system does not have any self-discharge, as the electrolytes cannot react when they are stored separately. This is an important advantage in situations where electricity is stored for longer durations.

Table 2 shows most important characteristics of flow batteries compared to other storage systems. This table shows that flow batteries are attractive for use in large-scale applications with large power ratings AND large energy ratings.

	Typical Power	**Typical Energy**	**Typical duration discharge**	**Maturity**
Batteries (lead-acid, NiCd, NiMH, Li-ion)	kW – 500 kW	MWh – 100 MWh	1 h – 8 h	Mature
Flywheels	500 kW – 1 MW	100 kWh – 100 MWh	< 5 minutes	Mature
Pumped hydro	100 MW – 4000 MW	500 MW - 15 GWh	4 – 12 h	Mature
CAES	25 MW – 3000 MW	200 MWh - 10 GWh	1 – 20 hours	Developed, first generation demonstrated
NaS	1 MW	1 MWh	1 hour	Developed, stage of demonstration projects finished, commercially available
SMES	10 kW – 10 MW	10 kWh – 1 MWh	1 – 30 minutes	Developed, not commercial yet
Supercapacitors	< 250 kW	10 kWh	< 1 minute	Developed
Flow batteries	100 kW – 10 MW	1 – 100 MWh	10 hours	Developed, stage of demonstration projects
Hydrogen storage	10 MW	unlimited	> 5 hours	Developing

Table 2. Overview of characteristics of different storage systems

Comparison of three types of flow batteries

Hence, flow batteries are especially interesting for use in large-scale applications, with specific requirements to power rating and energy rating and in situations that require a fast system. The three current systems all have their own specifications. In theory, all systems can be used for all sizes, but the manufacturers and developers each focus on a specific range of power and energy. PSB focuses on multi-MW systems, while vanadium and ZnBr have a typical range below 1 MW. As a consequence, PSB has to be built as a turnkey system, while the other two systems try to develop modular systems. But in principle all technologies can be produced on a large scale as well as a smaller scale. See Table 3 for a comparison of the three types of flow batteries.

	Vanadium	Zinc bromine	PSB
Typical power range (MW_e) [2]	< 3	< 1	< 15
Typical size range (MWh) [3]	0,5 – 5	0,01 – 5	0 - 120
Energy density (Wh/liter) [1]	16 - 33	60 – 90	20 - 30
Cycle efficiency [Wh^{out}/Wh^{in}] (%) [1, 2]	70 – 85	65 – 75	60 – 75
Cycle life (cycles) [1]	>12,000	>2,000	n/a
Life time (years) [1]	5 – 10	5 – 10	15
Stage of development [2]	Demonstration / commercial units	Demonstration / commercial units	Demonstration
Companies involved [3]	VRB, SEI, Pinnacle, Cellenium	ZBB, Premium Power	TVA, VRB (using Regenesys technology)

Table 3. Comparison of flow batteries, based on current status

Costs

The three types of flow batteries are in a roughly equivalent range of costs of the total system per kW. For initial systems this is several thousands of euros per kW, decreasing towards approximately € 1500 / kW and € 200 / kWh. For upscaling of the system the costs of the electrolytes are very important. ZnBr has the lowest electrolyte costs (20 €/kWh) and therefore appears very attractive for large-scale applications, but e.g. V/V systems (~ 50 €/kWh) offer greater scalability of the electrolyte storage. As soon as these systems are on the market as a mass-produced article, prices will decrease to a lower level of approximately 500 €/kW and 100 €/kWh.

Based on the longer cycle life of flow batteries, the flow batteries offer better life cycle costs than conventional batteries. But this claim is based on relatively little experience. So the technology should first prove itself to gain the market's confidence.

Compared to other technologies, flow batteries are relatively cheap, especially considering their good performance. Figure 3 gives a rough comparison of the capital costs of several electricity storage systems. As the costs highly depend on the dimensions of the system, the ranges of the costs are large and this figure can only be used for a rough indication of the costs.

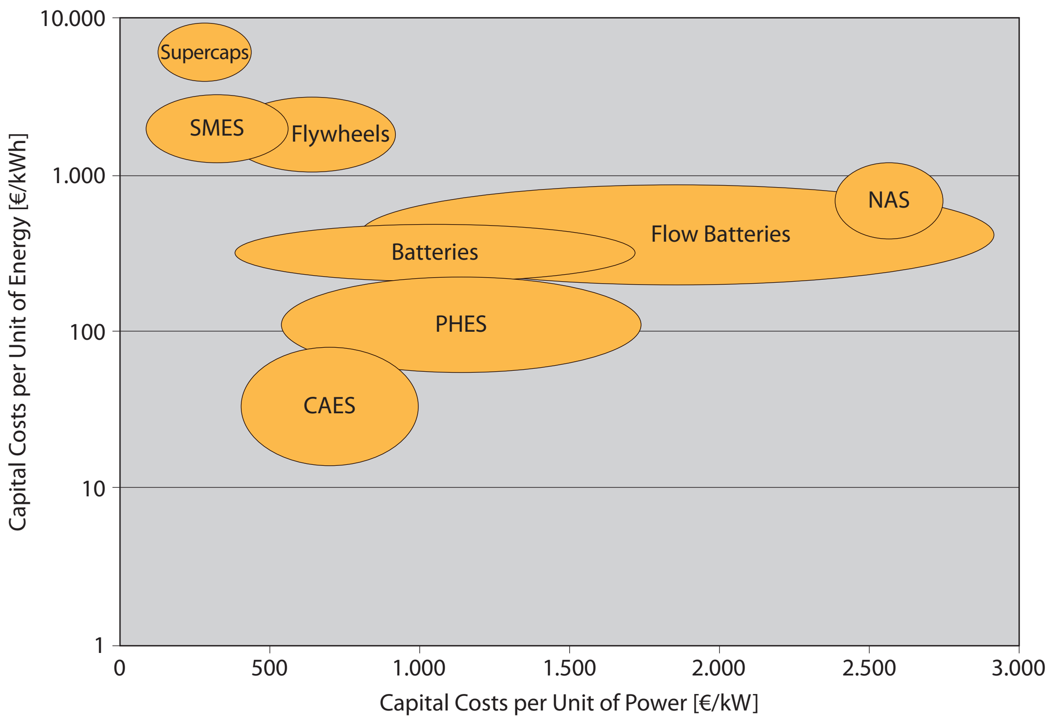

Figure 3. Rough comparison between current costs of storage systems

Applications

Based on the technology, flow batteries are very interesting for long-term storage. They can provide high-power and high-capacity discharge and can cycle very rapidly and deeply, without significant self-discharge. Due to the rapid response and the low operating costs when idle, flow batteries are well suited for services such as voltage and frequency regulation, load leveling, spinning reserve and stabilization of the output of renewable energy sources, e.g. peak power support at wind farms. Flow batteries are already demonstrated for several of these applications.

Table 4 gives an overview of most promising storage systems for different applications for electricity storage systems. Pumped hydro and CAES require large geographical impact storage capacities. Hydrogen storage (electrolysis of water into hydrogen in combination with a fuel cell or combustion engine) has a low round-trip efficiency and is therefore often not attractive. Batteries have a relatively high self-discharge. Moreover, the life time costs are higher than those of flow batteries. The other systems are especially attractive for short discharge times. This shows why for many applications flow batteries are seriously considered and very attractive.

Application	Specifications	Most important storage systems
Power quality	< 1 MW, 1 sec	Supercapacitors, SMES, flywheels, batteries
Energy management (long-term fluctuations, load leveling)	10-100 MW, 1-10 h	Pumped hydro, CAES, batteries, flow batteries, NaS, H_2 storage
Integration renewable energy sources	0,1 MW – 100 MW, 1 min – 10 hours	Flywheel, batteries, flow batteries, NaS
Back-up renewable energy sources	~1 MW, 1-20 hours	Pumped hydro, CAES, batteries, flow batteries. NaS
Peak generation	~1 MW, ~1 hour	Pumped hydro, CAES, flywheels, batteries, flow batteries, NaS
transmission stability	1-100 MW, 1 sec	SMES, batteries, flow batteries, NaS

Table 4. Overview of some applications of storage systems [1, 2, 3]

Current projects

Presently flow batteries are demonstrated in several projects and the first commercial projects are announced. A short description is given for each type of flow battery. As the flow battery is especially attractive for use in large-scale applications, this description focuses on these applications. For real-time and short notice support and optimization, applications have been limited to pumped hydro systems and some conventional lead-acid or nickel cadmium batteries, primarily due to a lack of cost-effective options.

PSB

The PSB technology is demonstrated in the Regenysis project for load leveling. However, this project was stopped, so it never proved the technology on a large scale. A second demonstration plant was built by TVA in Mississippi and was also canceled. This is a reconstruction of the first plant, to deliver electricity during peaking needs, improve power quality and reliability and to provide rapid response to changing power demand.

Other possible systems for energy storage in such specific situations, like PHES and CAES, required very large sites that were not available near the point of need and had negative environmental and financial impacts. Also NaS, V/V and Zn/Br were rejected based on the life-cycle costs. At the moment no large-scale demonstration projects are announced.

V/V

The V/V technology is already used in several small-scale applications. An example of a larger application is a 2 MWh system in Castle Valley Utah to supply peak power capacity. This is the first commercial large-scale project. VRB recently signed a deal to supply a 1.5 MW / 12 MWh system for a wind farm in Ireland. Due to the deep cycling in wind applications, conventional batteries are not suitable.

ZnBr

With ZnBr the experiences of ZBB are all on a small scale (<0.5 MWh). Due to the small scales of these projects, ZBB already has several projects running. ZBB offers these systems as a turn-key product and therefore focuses on small-scale applications.

Conclusion

The application of flow batteries offers many opportunities, especially in large-scale grid-connected applications. The first demonstration projects have demonstrated the technology on a large scale, but for characteristics like life time the technology first has to prove itself in the coming years. Based on the expected life time costs, it is a very attractive solution with both economical and technical benefits compared to the alternatives.

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