Evolving Energy Pty Ltd
PO Box 1131
Mullumbimby
NSW 2482
0487 701 710
ACN 169 512 930
ABN 91 169 512 930
contact@evolvingenergy.com.au

Flow Battery Overview

A flow battery, or redox flow battery (after reduction–oxidation), is a type of rechargeable battery where rechargeability is provided by two chemical components dissolved in liquids contained within the system and separated by a membrane.[1] Ion exchange (providing flow of electric current) occurs through the membrane while both liquids circulate in their own respective space. Cell voltage is chemically determined by the Nernst equation and ranges, in practical applications, from 1.0 to 2.2 volts.

A flow battery is technically akin both to a fuel cell and an electrochemical accumulator cell (electrochemical reversibility). While it has technical advantages such as potentially separable liquid tanks and near unlimited longevity over most conventional rechargeables, current implementations are comparatively less powerful and require more sophisticated electronics

Construction Principle

A flow battery is a rechargeable fuel cell in which an electrolyte containing one or more dissolved electroactive elements flow through an electrochemical cell that reversibly converts chemical energy directly to electricity (electroactive elements are "elements in solution that can take part in an electrode reaction or that can be adsorbed on the electrode"[2]). Additional electrolyte is stored externally, generally in tanks, and is usually pumped through the cell (or cells) of the reactor, although gravity feed systems are also known.[3] Flow batteries can be rapidly "recharged" by replacing the electrolyte liquid (in a similar way to refilling fuel tanks for internal combustion engines) while simultaneously recovering the spent material for re-energization.

In other words, a flow battery is just like an electrochemical cell, with the exception that the ionic solution (electrolyte) is not stored in the cell around the electrodes. Rather, the ionic solution is stored outside of the cell, and can be fed into the cell in order to generate electricity. The total amount of electricity that can be generated depends on the size of the storage tanks.

Types

Different classes of flow cells (batteries) have been developed, including redox, hybrid and membraneless. The fundamental difference between conventional batteries and flow cells is that energy is stored as the electrode material in conventional batteries but as the electrolyte in flow cells.

Redox

The redox (reduction–oxidation) cell is a reversible fuel cell in which all electrochemical components are dissolved in the electrolyte. The energy capacity of the redox flow battery is fully independent of its power, because the energy available is related to the electrolyte volume (amount of liquid electrolyte) and the power to the surface area of the electrodes. Redox flow batteries are rechargeable (secondary cells).[4] Because they employ heterogeneous electron transfer rather than solid-state diffusion or intercalation they are more appropriately called fuel cells than batteries. In industrial practice, fuel cells are usually, and unnecessarily, considered to be primary cells, such as the H2/O 2 system. The unitized regenerative fuel cell on NASA's Helios Prototype is another reversible fuel cell. The European Patent Organisation classifies redox flow cells (H01M8/18C4) as a sub-class of regenerative fuel cells (H01M8/18). Examples of redox flow batteries are the Vanadium redox flow battery, polysulfide bromide battery (Regenesys), and uranium redox flow battery.[5] Redox fuel cells are less common commercially although many systems have been proposed.[6][7][8][9]

Researchers announced a prototype, zinc-polyiodide flow battery with an energy density of 167 Wh/l (watt-hours per liter). Older zinc-bromide cells reach 70 Wh/l. For comparison, lithium iron phosphate batteries that store 233 Wh/l.

The zinc-polyiodide battery is claimed to be safer than other flow batteries given its absence of acidic electrolytes, nonflammability and operating range of −4 to 122 °F (−20 to 50 °C) that does not require extensive cooling circuitry, which would add weight and occupy space. One unresolved issue is zinc build-up that grew from the negative electrode and permeated the membrane, reducing efficiency. Adding alcohol to the electrolyte contained the problem.[10]

When the battery is fully discharged, both tanks hold the same electrolyte solution: a mixture of positively charged zinc ions (Zn2+) and negatively charged iodide ion, I-. When charged, one tanks holds another negative ion, polyiodide, I3- The battery produces power by pumping liquid from external tanks into the battery's stack area where the liquids are mixed. Inside the stack, zinc ions pass through a selective membrane and change into metallic zinc on the stack's negative side.[11]

Hybrid

The hybrid flow battery uses one or more electroactive components deposited as a solid layer.[12] In this case, the electrochemical cell contains one battery electrode and one fuel cell electrode. This type is limited in energy by the surface area of the electrode.

Hybrid flow batteries include the zinc-bromine, zinc–cerium[13] and lead–acid flow batteries.

Membraneless

This battery employs a phenomenon called laminar flow in which two liquids are pumped through a channel. They undergo electrochemical reactions to store or release energy. The solutions stream through in parallel, with little mixing. The flow naturally separates the liquids, eliminating the need for a membrane.[14]

Membranes are often the most costly component and the most unreliable components of batteries, as they can corrode with repeated exposure to certain reactants. The absence of a membrane enabled the use of a liquid bromine solution and hydrogen. This combination is problematic when membranes are used, because they form hydrobromic acid that can destroy the membrane. Both materials are available at low cost.[15]

The design uses a small channel between two electrodes. Liquid bromine flows through the channel over a graphite cathode and hydrobromic acid flows under a porous anode. At the same time, hydrogen gas flows across the anode. The chemical reaction can be reversed to recharge the battery—a first for any membraneless design.[15] One such membraneless flow battery published in August 2013 produced a maximum power density of 7,950 W/m^2, three times as much power as other membraneless systems— and an order of magnitude higher than lithium-ion batteries.[15]

Organic

In 2013, researchers announced the use of 9,10-anthraquinone-2,7-disulphonic acid (AQDS), a quinone, as a charge carrier in metal-free flow batteries. Each of the carbon-based molecules holds two units of electrical charge, compared with one unit in conventional batteries, implying that a battery could store twice as much energy in a given volume.[16] AQDS undergoes rapid, reversible two-electron/two-proton reduction on a glassy carbon electrode in sulphuric acid. An aqueous flow battery with inexpensive carbon electrodes, combining the quinone/hydroquinone couple with the Br2/Br− redox couple, yields a peak galvanic power density exceeding 6,000 W/m^2 at 13,000 A/m^2. Cycling showed >99 per cent storage capacity retention per cycle. Volumetric energy density was over 50 Wh/l and specific energy density over 50 Wh/kg.[17] The organic anthraquinone species can be synthesized from inexpensive commodity chemicals. This organic approach permits tuning of the reduction potential and solubility by adding functional groups. Adding two hydroxy groups to AQDS increases the open circuit potential of the cell by 11%.[18]

In 2014, another example used anthraquinone-2-sulfonic acid or anthraquinone-2,6-disulfonic acid on the negative side and 1,2-dihydrobenzoquinone- 3,5-disulfonic acid on the positive side. The battery was claimed to last for 5,000 cycles without degradation.[19]

Metal Hydride

Proton flow batteries integrate a metal hydride storage electrode into a reversible proton exchange membrane (PEM) fuel cell. During charging, PFB combines hydrogen ions produced from splitting water with electrons and metal particles in one electrode of a fuel cell. The energy is stored in the form a solid-state metal hydride. Discharge produces electricity and water when the process is reversed and the protons are combined with ambient oxygen. Metals less expensive than lithium can be used and provide greater energy density than lithium cells.[20][21]

Nano-Network

In 2014 a technology was announced that uses lithium–sulfur chemistry arranged in a network of nanoparticles. The network eliminates the requirement that charge moves in and out of particles that are in direct contact with a conducting plate. Instead, the nanoparticle network allows electricity to flow throughout the liquid. This allows more energy to be extracted.[22]

In August 2014, the Quant e-Sportlimousine was approved for testing on public roads using the nanoFLOWCELL® system with a claimed energy or power density of 600 Wh per kilogram (per litre of salt water electrolyte).[23]

Semi-Solid

In a semi-solid flow cell, the positive and negative electrodes are composed of particles suspended in a carrier liquid. The positive and negative suspensions are stored in separate tanks and pumped through separate pipes into a stack of adjacent reaction chambers, where they are separated by a barrier such as a thin, porous membrane. The approach combines the basic structure of aqueous-flow batteries, which use electrode material dissolved in a liquid electrolyte, with the chemistry of lithium-ion batteries. Dissolving a material changes its chemical behavior significantly. However, suspending bits of solid material preserves the solid's characteristics. The result is a viscous suspension that flows like molasses.[24]

Chemistries

There are a wide range of chemistries that have been trialled for flow batteries.[1]

Couple	**Max. cell voltage (V)**	**Average electrode power density (W/m^2)**	**Average fluid energy density (W·h/kg)**
Hydrogen–lithium bromate	1.1	15,000	750
Hydrogen–lithium chlorate	1.4	10,000	1400
Bromine-hydrogen	1.07	7,950	
Iron–tin	0.62	<200	
Iron–titanium	0.43	<200	
Iron–chrome	1.07	<200	
Vanadium–vanadium (sulphate)	1.4	~800	25
Vanadium–vanadium			50

Couple	Max. cell voltage (V)	Average electrode power density (W/m^2)	Average fluid energy density (W·h/kg)
(bromide)			
Sodium–bromine polysulfide	1.54	~800	
Zinc–bromine	1.85	~1,000	75
Lead–acid (methanesulfonate)	1.82	~1,000	
Zinc–cerium (methanesulfonate)	2.43	<1,200–2,500	

Advantages And Disadvantages

Redox flow batteries, and to a lesser extent hybrid flow batteries, have the advantages of flexible layout (due to separation of the power and energy components), long cycle life (because there are no solid-to-solid phase transitions), quick response times, no need for "equalisation" charging (the over charging of a battery to ensure all cells have an equal charge) and no harmful emissions. Some types also offer easy state-of-charge determination (through voltage dependence on charge), low maintenance and tolerance to overcharge/overdischarge.

On the negative side, flow batteries are rather complicated in comparison with standard batteries as they may require pumps, sensors, control units and secondary containment vessels. The energy densities vary considerably but are, in general, rather low compared to portable batteries, such as the Li-ion.

Applications

Flow batteries are normally considered for relatively large (1 kWh – 10 MWh) stationary applications. These are for;

- Load balancing – where the battery is connected to an electrical grid to store excess electrical power during off-peak hours and release electrical power during peak demand periods. The common problem limiting the use of most flow battery chemistries in this application is their low areal power (operating current density) which translates into a high cost of power.
- Storing energy from renewable sources such as wind or solar for discharge during periods of peak demand.[25]
- Peak shaving, where spikes of demand are met by the battery.[26]
- UPS, where the battery is used if the main power fails to provide an uninterrupted supply.
- Power conversion – because all cells share the same electrolyte/s. Therefore, the electrolyte/s may be charged using a given number of cells and discharged with a different number. Because the voltage of the battery is proportional to the number of cells used the battery can therefore act as a very powerful DC–DC converter. In addition, if the number of cells is continuously changed (on the input and/or output side) power conversion can also be AC/DC, AC/AC, or DC–AC with the frequency limited by that of the switching gear.[27]
- Electric vehicles – Because flow batteries can be rapidly "recharged" by replacing the electrolyte, they can be used for applications where the vehicle needs to take on energy as fast as a combustion engined vehicle.[28][29] A common problem found with most RFB chemistries in the EV applications is their low energy density which translated into a short driving range.
- Stand-alone power system – An example of this is the telecom industry for use in cellphone base stations where there is no grid power available. The battery can be used alongside solar or wind power sources to compensate for their fluctuating power levels and alongside a generator to make the most efficient use of it to save fuel.[30][31]

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