

Redox Flow Batteries

Principle

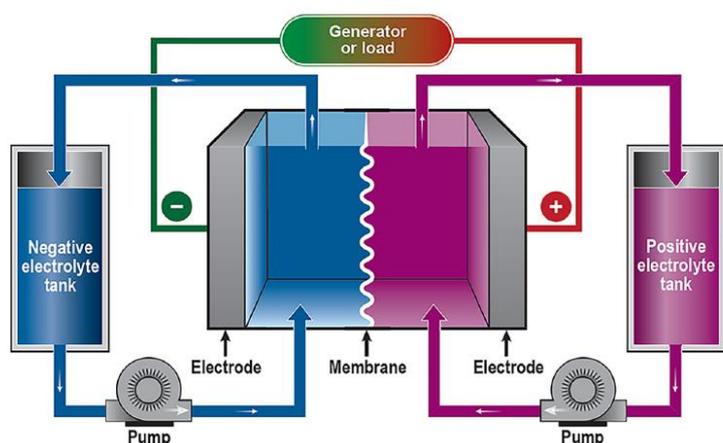


Figure 1. Scheme of a RFB having two tanks for electrolytes and one electrochemical cell with two compartments separated by an ion selective membrane. Image from [1].

Redox Flow Batteries (RFBs) are an innovative technology in which the electroactive materials are not fixed to the electrodes but dissolved in the electrolytes. As shown in Figure 1, the energy is stored/delivered when the active materials flow through positive and negative chambers that are separated by an ion exchange membrane and undergo redox reactions at electrode-electrolyte interface. Electrolytes are stored in separate tanks and supplied to the electrochemical reactor on demand, leading to the effective decoupling of energy and power. Energy is determined by the amount of charge stored in the electrolytes (which depends on the number of electrons transferred and the concentration of active species) and the cell voltage (determined by the thermodynamics of the electrochemical reactions). Power depends on the electrode active area inside the stack of cells and the operating current density.

Characteristics

RFBs offer several advantages over conventional batteries. Design flexibility is a major advantage, in which the energy (the volume of electrolyte in external tanks) and power output (the active area inside stacks) are effectively decoupled and can be adjusted to meet the demands of the end users [2]. This property makes flow-battery technology attractive for storage applications with a large Energy-to-Power ratio.

Main function

- Expand deployment of renewable power plants.
- Peak load shifting.
- Grid stabilization.
- Power quality in distribution networks.

A second advantage is that the redox reactions occur on the electrode surface without damaging the internal structure, thus making it more suitable for long cycle life. Additionally, the possibility of ultra-fast mechanical charging by substituting spent electrolytes with fresh ones is a differentiating characteristic that avoids the destructive effects of fast electrical charging.

General performance

- Typical Power: 1 to 200 MW
- Cycle efficiency: 70 - 80 %
- Discharge time: ≥ 4 hours
- Response time: 0.1 – 0.2 s
- Cycle life: $> 10,000$ cycles
- Technical lifetime: > 20 y
- Energy to Power ratio: $\geq 4/1$

The unique plate and frame architecture of the flow battery offer a further advantage. This design shifts the manufacturing approach away from the expensive electrode-preparation steps of Lithium-ion batteries, thereby enabling the cost-effective scaling of flow batteries for large storage systems [3]. This architecture also facilitates dismantling and separating most of the internal components of the stack for further reuse or recycling. Because the electrolyte is not consumed, it can be easily recycled to produce other electrolytes or raw materials after the end of battery's lifetime.

■ Maturity Level

Maturity Level:

Installed rated power worldwide: 325 MW

Installation costs: depend on E/P ratio
300 €/kWh (E/P=4) to 2000 €/kWh (E/P=0.25)

Operating costs: 2 - 3% investment + cost of energy inefficiencies

RFBs are in early commercialization stage with just 23 plants installed worldwide with rated power over 1 MW each[4]. An example is shown in Figure 2. The most studied and advanced RFB technology is the Vanadium Redox Flow Battery (VRFB), based on V(II)/V(III) and V(IV)/V(V) redox reactions in acidic media. The largest planned battery in the world is a 200MW/800MWh VRFB being manufactured in Dalian, China, by Rongke Power [5]. So far, system installed costs of VRFBs are substantially higher than the U.S. Department of Energy cost target of 100 \$/kWh. This applies even for large Energy-to-Power ratios, which are beneficial to reduce investment cost. For example, Crawford et al [6] estimated 325 \$/kWh for E/P= 4 and 200 \$/kWh for E/P=10.

Operating costs of RFBs are mostly determined by the cost of electricity and the round-trip cycle efficiency of the battery, which is around 80%. This value is low compared to

Lithium-ion batteries that usually go over 90%. However, energy expenditure to cool the Lithium-ion battery system to reduce the risk of fire can consume a significant amount of energy and drastically decrease the global energy efficiency. In this sense, cooling flow batteries is simpler and more efficient than cooling Lithium-ion batteries. Unlike Lithium-ion batteries, RFBs may involve maintenance costs such as substitution of membranes, felts, bipolar plates, and repairing piping and pumps. Annual maintenance costs account for about 2 - 3% of the total initial investment.



Figure 2. 2MW/8MWh VRFB demonstration system at Yokohama, Japan. Picture from [7].

■ Potential, barriers and challenges

Traditional inorganic-based materials encounter critical technical and economic limitations such as low solubility, low operation potential, inferior electrochemical activity, and high cost. Redox-active organic materials (ROMs) are promising alternative “green” candidates to push the boundaries of energy storage because of the significant advantages of molecular diversity, structural tailorability, and natural abundance [1]. A growing area of interest involves engineering the structure of organic redox molecules to capture the best combination of the most attractive properties [3]. Regardless of the chemical nature of the redox material, all RFBs rely on expensive and poor performing ion-selective membranes to keep positive and negative electrolytes physically separated but electrochemically connected through ion conduction. Cost analyses show that the membranes contribute 10 to 20% of the total cost (depending on the E/P ratio). Several strategies have been applied to avoid ion-exchange membranes. Using large organic molecules or even polymers will open the possibility to use low cost size exclusion membranes. Membrane-less concepts require at least one active species to be a solid [8], operate with the ideal laminar flow characteristics of microfluidic systems, or make use of immiscible electrolytes that spontaneously form an interphase that functions as a physical barrier [9].

Potential

- Design flexibility
- Long cycle life and life-time
- Capacity scalability
- Recyclability

Barriers

- Emerging technology
- High investment costs
- BoP complexity

Challenges

- Increase energy density
- Increase round-trip efficiency
- Reduce cost
- Avoid critical materials

References

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