Flow Batteries

by Trung Nguyen and Robert F. Savinell

Renewable energy sources including wind and solar can supply a significant amount of electrical energy in the United States and around the world. However, because of their intermittent nature, the potential of these two energy sources can be fully exploited only if efficient, safe, and reliable electrical energy storage (EES) systems are provided. EES will also be critical to improving the robustness and efficiency of the grid by reducing power surges and balancing the load over time. A recent report from Sandia identifies over 17 major opportunities of EES to make an impact on the U.S. grid and implementation of renewables.[1] For very large energy storage applications, only pumped hydro and compressed gas are cost effective at this time. These technologies, however, are limited by geography, while electrochemical energy storage devices such as batteries, fuel cells/flow batteries, and electrochemical capacitors are among the leading EES technologies for the future because of their scale-ability and versatility. Their power and energy density characteristics are shown in Fig. 1.[2] Capacitors, with their very high power densities, low energy densities, and sub-second response times, are more suitable for power quality management. Batteries and flow batteries/fuel cells have the energy densities needed for large-scale electrical energy storage.

Batteries and flow batteries/fuel cells differ in two main aspects. First, in a battery, the electro-active materials are stored internally, and the electrodes at which the energy conversion reactions occur are themselves part of the electrochemical fuel. The characteristics of the negative and positive electrodes determine both the power density (*e.g.*, electrical, transport, and catalytic properties of the active material and non-reactive materials) and the energy density (*e.g.*, mass of active materials) of the battery. As a battery converts its chemical energy to electrical energy, electrodes are consumed and undergo significant physical and chemical changes which affect its electrical performance. Second, because of the dual functions of the electrodes described above, a conventional battery has minimal or no scale-up advantages. Instead, it can only be scaled-out. That is, if more energy is needed, then more battery modules with identical components are required. As the amount of electro-active materials increases in a battery, more current collecting materials, electrolyte, separators, and enclosure materials are also needed. Consequently, a battery can never approach its theoretical energy density. Furthermore, increasing the capacity of a battery almost always increases internal resistances and consequently decreases power density and efficiency.

Flow Batteries Classification

A flow battery is an electrochemical device that converts the chemical energy in the electro-active materials directly to electrical energy, similar to a conventional battery and fuel cells. The electro-active materials in a flow battery, however, are stored mostly externally in an electrolyte and are introduced into the device only during operation.[3] True flow batteries have all the reactants and products of the electro-active chemicals stored external to the power conversion device. Systems in which all the electro-active materials are dissolved in a liquid electrolyte are called redox (for reduction/oxidation) flow batteries (RFBs). A schematic of a redox flow battery system is shown in Fig. 2. Other true flow batteries might have a gas species (*e.g.*, hydrogen, chlorine) and liquid species (*e.g.*, bromine). Rechargeable fuel cells like H_2-Br_2 and H_2-Cl_2 could be thought of as true flow batteries. Systems in which one or more electro-active components are stored internally are called hybrid flow batteries. Examples include the zinc–bromine and zinc–chlorine batteries. Similarly to conventional batteries, the energy densities of these hybrid flow batteries are limited by the amount of electro-active materials that can be stored within the batteries and they have limited scale-up advantages. Table I shows some of the more well-known flow battery systems. Although much flow battery research dates back to the 1970s, some research has continued over the past several decades and the state-of-the art has been reviewed in the recent literature.[4]

Most redox flow batteries consist of two separate electrolytes, one storing the electro-active materials for the negative electrode reactions and the other for the positive electrode reactions. (To prevent confusion, the negative electrode is the anode and the positive electrode is the cathode during discharge. It is understood that they will be reversed during charge.) Both the fresh and spent electrolytes may be circulated and stored in a single storage tank as shown in Fig. 2 or separately to control the concentrations of the electro-active material. An ion selective membrane is often used to prevent mixing or cross-over of the electro-active species which result in chemical short-circuit of electro-active materials. Only the common counter ion carrier is allowed to cross the membrane. For example, in the bromine-polysulfide system, as Na_2S_2 is converted to Na_2S_4 at
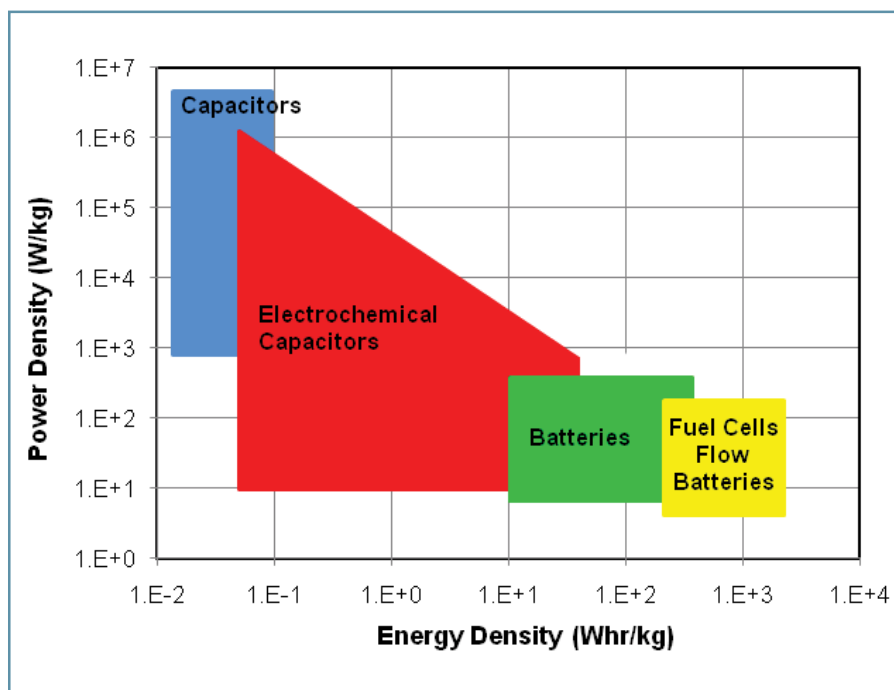

Fig. 1. *Power and energy densities of various EES systems.*

the anode and Br_2 is converted to $2Br^-$ at the cathode, the excess Na^+ ions at the anode are allowed to cross to the cathode to maintain electroneutrality condition. Similarly, in the vanadium system, as V^{+2} is oxidized to V^{+3} at the anode and V^{+5} is reduced to V^{+4} at the cathode, hydronium ions are transported across a proton conducting membrane from the anode to the cathode. In this case, however, sometimes a microporous non-selective membrane separator can be used since most of the current might be carried by high mobility protons in the acid electrolyte and since the cross-over of the common vanadium cation lowers efficiency but does not cause a permanent loss of capacity. (Note: the distinction of the flow electrolyte does not take into account the fixed electrolyte within the membrane separator of many flow batteries.)

A fuel cell might be considered as a type of flow battery in that the power conversion component is independent of the chemical energy capacity of the device. Most fuel cells, however, cannot be reversed electrically efficiently, and therefore cannot be used effectively as an electrical energy storage device; so they are considered as a chemical energy conversion device only.

Advantages and Disadvantages

With the electrolyte and electro-active materials stored externally, true flow batteries have many advantages, one of which is the separation of the power and energy requirements. The electrodes, not being part of the electrochemical fuel, can be designed to have optimal power acceptance and delivery properties (*e.g.*, catalytic, electrical, and transport) without the need to also maximize energy storage density. Furthermore, the electrodes do not undergo physical and chemical changes during operation (because they do not contain active materials), thus leading to more stable and durable performance. Therefore, engineered microstructures developed to optimize performance can be maintained over the lifetime of the device: with longer lifetimes, the capital costs of the battery system can be amortized over a longer period, and with a wider state-of-charge operating window, the quantity of active material required to deliver power over the entire required duration of discharge can be minimized.

The energy capacity requirement of a flow battery is addressed by the size of the external storage components. Consequently, a redox flow battery system could approach its theoretical energy density as the system is scaled up to a point where the weight or volume of the battery is small relative to that of the stored fuel and oxidant. A conventional analogous system is the internal combustion engine system in which the power is determined by

Table I. Characteristics of Some Flow Battery Systems.			
System	**Reactions**	$E_{cell}{}^o$	**Electrolyte**
Redox			Anode/Cathode
All Vanadium [3]	Anode: $V^{2+} \xleftrightarrow{charge \; discharge} V^{3+} + e-$ Cathode: $VO_2^+ + e- \xleftrightarrow{charge \; discharge} VO^{2+}$	1.4 V	H_2SO_4/H_2SO_4
Vanadium-Polyhalide [5]	Anode: $V^{2+} \xleftrightarrow{charge \; discharge} V^{3+} + e-$ Cathode: $½ Br_2 + e- \xleftrightarrow{charge \; discharge} Br^-$	1.3 V	VCl_3-HCl/NaBr-HCl
Bromine-Polysulfide [6]	Anode: $2 S_2^{2-} \xleftrightarrow{charge \; discharge} S_4^{2-} + 2e-$ Cathode: $Br_2 + 2e- \xleftrightarrow{charge \; discharge} 2 Br^-$	1.5 V	$NaS_2/NaBr$
Iron-Chromium [7]	Anode: $Fe^{2+} \xleftrightarrow{charge \; discharge} Fe^{3+} + e-$ Cathode: $Cr^{3+} + e- \xleftrightarrow{charge \; discharge} Cr^{2+}$	1.2 V	HCl/HCl
H_2-Br_2 [8]	Anode: $H_2 \xleftrightarrow{charge \; discharge} 2H^+ + 2e-$ Cathode: $Br_2 + 2e- \xleftrightarrow{charge \; discharge} 2Br^-$	1.1 V	PEM*- HBr
Hybrid			
Zinc-Bromine	Anode: $Zn \xleftrightarrow{charge \; discharge} Zn^{2+} + 2e-$ Cathode: $Br_2 + 2e- \xleftrightarrow{charge \; discharge} 2 Br^-$	1.8 V	$ZnBr_2/ZnBr_2$
Zinc-Cerium [9]	Anode: $Zn \xleftrightarrow{charge \; discharge} Zn^{2+} + 2e-$ Cathode: $2Ce^{4+} + 2e- \xleftrightarrow{charge \; discharge} 2Ce^{3+}$	2.4 V	CH_3SO_3H (both sides)

*Polymer Electrolyte Membrane

the size of the engine and the energy density is determined by the size of the fuel tank.

In a flow battery there is inherent safety of storing the active materials separately from the reactive point source. Other advantages are quick response times (common to all battery systems), high electricity-to-electricity conversion efficiency, no cell-to-cell equalization requirement, simple state-of-charge indication (based on electro-active concentrations), low maintenance, tolerance to overcharge and over-discharge, and perhaps most importantly, the ability for deep discharges without affecting cycle life. The hybrid systems like those involving zinc plating do not offer all these advantages, but still have many of the desirable features of a true flow battery. The main disadvantage of flow batteries is their more complicated system requirements of pumps, sensors, flow and power management, and secondary containment vessels, thus making them more suitable for large-scale storage applications.

If one examines the vanadium flow battery system, one of the few redox flow batteries that has been tested at the utility scale, one estimates that the vanadium itself is a significant cost driver: cost analysis suggests that the vanadium material contributes between $50/kWh to $110/kWh at current vanadium prices, or from 50 to 100 percent of the aforementioned cost target of $100-200/kWh. From this standpoint, identifying low-cost redox couples with high solubility is critical to meeting the ultimate market requirements.

The other key cost driver is the construction of the electrochemical cell itself. The construction costs of the cell scale with the total power requirement of the application, but these costs are directly rated to the specific power of the device itself–how effectively the materials are utilized. While flow batteries ought to be able to operate at relatively high current densities, as convection can be employed to deliver reactants to the electrode surface, flow batteries have typically been operated at ~50 mA/cm^2, a current density consistent with conventional batteries without convection. It is anticipated that electrolyte management and cell design can deliver at least a 5x improvement in power density, thereby reducing cell construction costs by close to that same factor of 5.

Current Technical Barriers

Only a few flow battery systems have seen deployment. Consequently, the technologies are relatively new and unfamiliar. Further development will
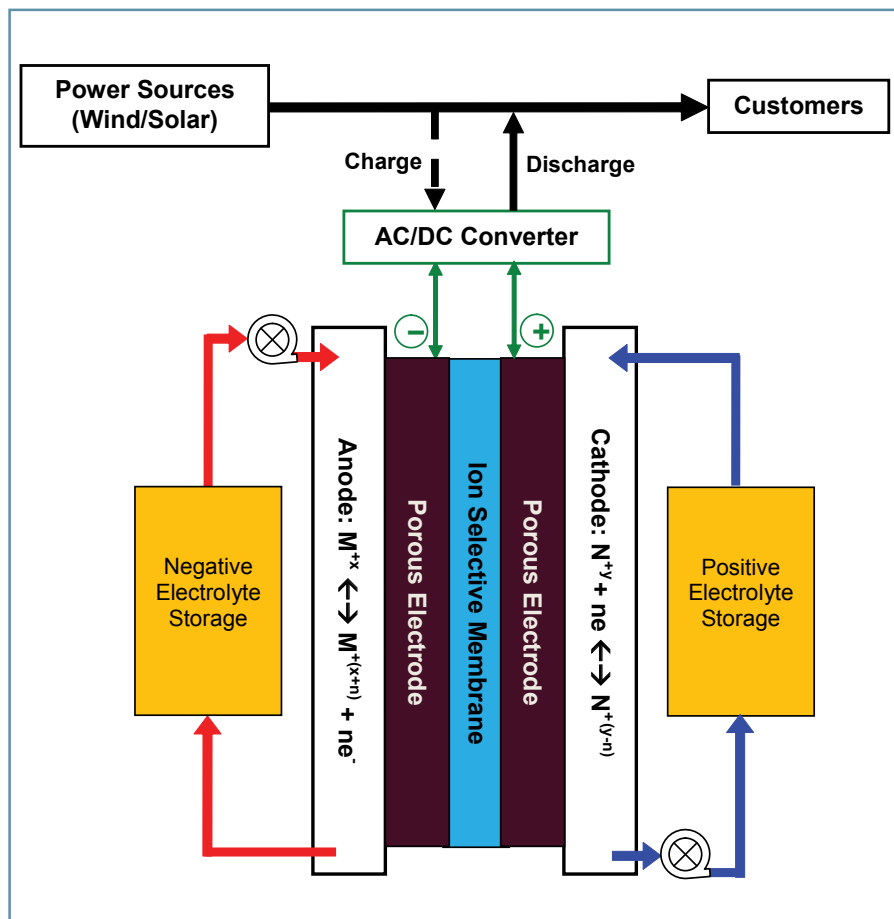
Fig. 2. *Schematic of a redox flow battery system with electrodes shown in a discharge mode.*

require research activities in the following areas: (1.) low-cost, efficient, and durable electrodes; (2.) chemically stable redox couples, having large potential differences, with high solubilities of both oxidized and reduced species, and fast redox kinetics; (3.) highly permselective and durable membranes; (4.) electrode structure and cell design that minimize transport losses; (5.) designs with minimal pumping and shunt current losses; and (6.) large scale power and system management and grid integration. Overall, the primary barriers to commercialization for large scale energy storage are round trip energy storage efficiency, cost for energy storage in terms of $/kwh, and cost for the power capacity in terms of $/kw. ■

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