



# Hawai'i Natural Energy Institute Research Highlights

## Electrochemical Power Systems

### Vanadium Flow Battery with High Concentration Electrolytes

**OBJECTIVE AND SIGNIFICANCE:** The objective of this research activity is to develop a high power and energy density, durable and safe vanadium flow battery (VFB) with novel catalysts and high concentration of vanadium electrolytes. The proposed research has the potential to double the energy density of vanadium electrolytes, and significantly improve the negative electrode performance. This work would facilitate the VFB system achieving the durability and cost required for large-scale energy storage applications.

**BACKGROUND:** A flow battery is an electrochemical device that comprises of a cell stack to reversibly convert the chemical energy of electrolytes to electricity, and external tanks to store the electrolytes containing redox-active species. The sizes of stack and tanks determine the power (kW) and the energy capacity (kWh) independently. The separation of energy storage from the electrochemical conversion unit enables the power and the energy capacity to be independently scaled up for the storages from a few hours to days, depending on the application. For large scale applications, flow batteries also have several key advantages compared to the traditional rechargeable (e.g. Li-ion and lead-acid) batteries, including longer operational lifetimes with deep discharge capabilities, simplified manufacturing, and improved safety characteristics.

To date, VFB is technically the most advanced system of the under-developing flow batteries. Due to it using only one element (vanadium) in both tanks, it overcomes cross-contamination degradation, a significant issue with other flow batteries that use more than one active element. The vanadium ions with oxidation states of 2+/3+ and 4+/5+ are used as active species in the negative and positive electrolytes respectively. The power density of VFBs depends on the redox reactions activities and the concentration of vanadium ions in the electrodes (graphite felts). The energy density is determined by the concentration of vanadium ions: the higher concentration, the higher energy density. The maximum concentration of electrolytes are limited by the solubility of  $\text{VOSO}_4$ , a starting electrolyte, and the stability of vanadium species. The solubility of  $\text{V}^{2+}$ ,  $\text{V}^{3+}$  and  $\text{VO}^{2+}(4+)$  decreases with increase of the sulfate concentration due to the common-ion effect; but the stability and solubility of  $\text{VO}_2^+(5+)$  increase with increase of the

acid concentration. Therefore, the concentration of sulfuric acid and vanadium is usually controlled at 2-4 M and 1-2 M, respectively, which is relatively low for the energy storage application. In addition, VFBs usually require expensive polymer membranes due to the highly acidic and oxidative environment, which lead to high system costs. The low energy densities, along with high capital cost, make it difficult for the current VFBs to meet the performance and economic requirements for broad market penetration. To reduce VFBs' cost, a number of research has been conducted, which aims to improve the vanadium electrolyte energy density and the system performance by increasing vanadium concentration.

Since late 2019, HNEI has conducted VFB research activities to improve the VFB performance and energy density. One of the efforts is diminishing the acid concentration in  $\text{V}^{2+}$ ,  $\text{V}^{3+}$ , and  $\text{VO}^{2+}$  electrolytes to increase the vanadium concentration. A novel electrochemical procedure has been developed to prepare a low acid and high vanadium ( $\text{V}^{3+}$ ) concentration negative electrolytes. The obtained negative electrolyte contains a maximum 5 M vanadium with  $\sim 0.1$  M  $\text{H}^+$ , and the positive electrolyte maximizes to  $\sim 3$  M vanadium. These increased vanadium concentrations in negative and positive electrolytes imply a potential double improvement of the energy density of vanadium electrolytes. The prepared electrolytes were used to validate the charge-discharge feasibility in a single cell with an anion exchange membrane (AEM) in the VFB instead of the conventional proton exchange membrane. The key features of a VFB cell with AEM are illustrated in Figure 1.

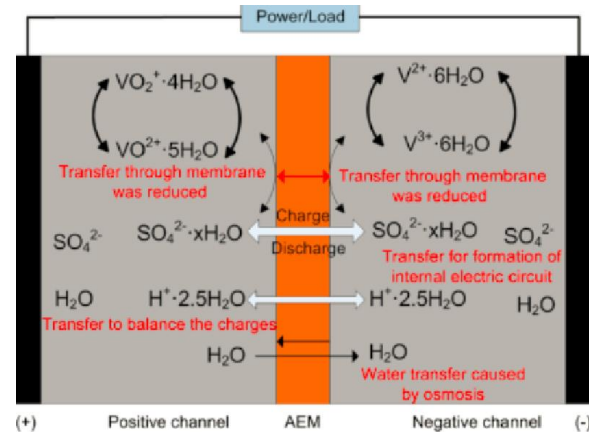


Figure 1. The features of a VFB cell with AEMs.

During the charge-discharge processes, vanadium redox reactions take place in negative and positive electrolytes; the bisulfate ions transport through AEM to form the internal electric circuit. Simultaneously, the sulfate and proton concentration variation also maintains the stability of the positive electrolyte. As shown in Figure 2, a single cell with 3 M vanadium electrolytes in both sides successfully demonstrates a good charge-discharge performance. Both positive and negative electrodes show low overpotentials. However, the low ionic conductivity of the AEM and the negative electrolytes, as well as the high proton permeability of the AEM result in large ohmic losses and a low energy efficiency. Furthermore, due to the poor AEM chemical and mechanical properties, the electrolytes leakage caused the operation failure during the second discharging.

Challenges were identified as the low chemical and mechanical stability and the high proton permeability of the AEMs, and the low ionic conductivity of the AEMs and the negative electrolytes. Currently, novel catalysts are being developed for the redox reactions of vanadium ions at negative electrode to further improve the power density of the high energy density VFBs.

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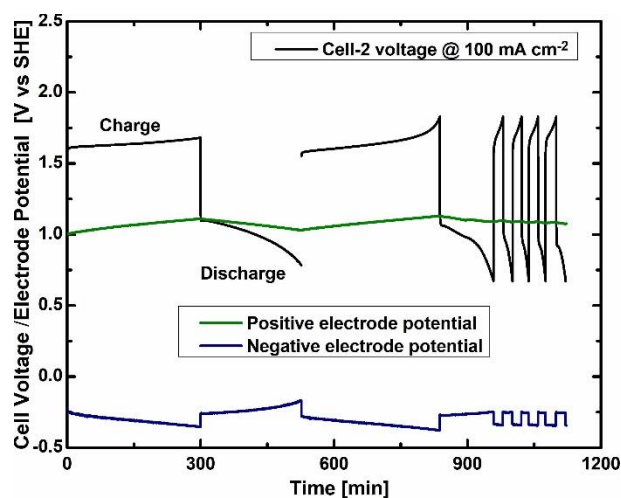


Figure 2. Charge-discharge cycles of VFB with an AEM and 3 M electrolytes in both sides.

**PROJECT STATUS/RESULTS:** An electrochemical procedure has been developed to prepare a low acid ( $H^+$  low to 0.1 M) and high vanadium concentration (V up to 5 M) negative electrolytes. The acid concentration decreases by a factor of more than 30 and the vanadium concentration doubled compared to the state of the art. Single cells operated with the high concentration vanadium electrolytes were evaluated with different AEMs and demonstrated good performance and low overpotentials for both positive and negative electrodes.