

## High Efficiency Vanadium-Metal Hydride Hybrid Flow Battery: Importance in Ion Transport and Membrane Selectivity

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Here, we combine the vanadium redox flow battery and the acid/alkaline hybrid battery concepts, and propose a novel flow Vanadium-Metal Hydride (V-MH) hybrid rechargeable battery. This V-MH flow battery system consists of graphite felt electrode (+ve) and a metal hydride electrode (-ve), operating in flowing  $V^{4+}/V^{5+}$ - $H_2SO_4$  aqueous solution and flowing KOH aqueous solution, respectively via a piece of membrane/separator (as shown in Fig. 1). This membrane should serve well as an ionic conductor and barrier. In principle, this hybrid battery system can provide an overall cell capacity of 110 mAh/g, cell voltage of 1.8 V, and a much higher energy density of 200 Wh/kg than that of the conventional all vanadium redox flow battery (60.5 Wh/kg as shown in Fig. 2). These promising characteristics prompt an excellent opportunity to apply this hybrid system as an effective energy storage system from intermittent energy sources like wind and solar power.

The membrane/separator in this hybrid system plays the most important role as it provides ionic conductivity for the charge carriers and prevents the crossover of the active ions. As an extended study of our previous reports,<sup>1-6</sup> the main objective of this work is to investigate the effect of different membrane (commercial monopolar membranes from Dupont, Fumatech and Membrane International, Ltd.) on the hybrid system as these membranes are made from different basic polymers, and contain various type and concentration of the fixed charged groups, with different levels of ion selectivity/permeability. Previously, we applied a bipolar membrane with a thickness of 1 mm to this hybrid system, and obtained a quite stable charge/discharge behavior. However, this bipolar membrane is the main component limiting the power density due to its thickness, resulting in a high internal resistance (voltage drop). It is believed that decreasing the thickness of the membrane effectively increases power density, but thinner membrane cannot prevent the ion crossover effectively.

We anticipated that using one monopolar membrane with thinner thickness (less than 0.5 mm) would be an alternate for the hybrid flow battery, thus increasing the limiting current density and leading to higher power density. Some surface modifications for the potential candidates will be done to avoid or minimize the ions crossover.

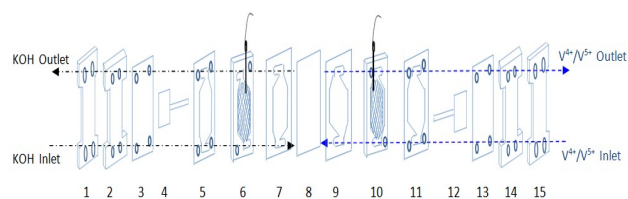


Fig. 1. Set-up and components of the V-MH hybrid flow battery. [1,15- Titanium endplates; 2,14- Polytetrafluoroethylene (PTFE) end frames; 3,5,7,9,11,13- Silicone gaskets; 4- Metal hydride electrode, negative electrode; 6,10- PTFE flow frame (integrated with Polyvinylidene Fluoride turbulence promoter) with integrated Hg/HgO and Hg/Hg<sub>2</sub>SO<sub>4</sub> reference electrodes, respectively; 8- membrane/separator; 12- Graphite felt electrode, positive electrode.]

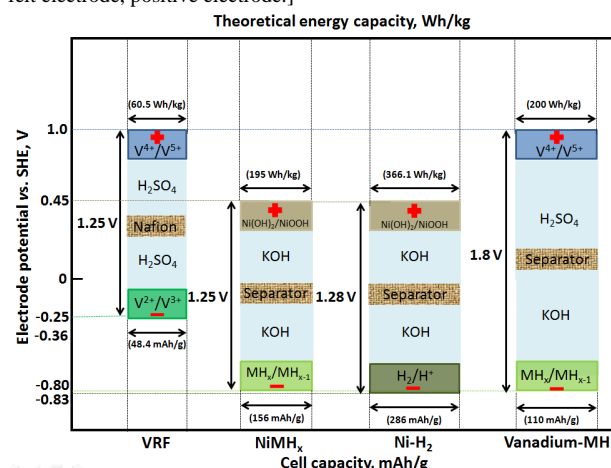
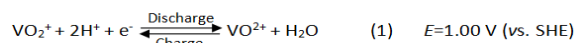


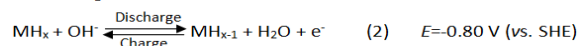
Fig. 2. Cell voltage, cell capacity and specific energy of different batteries pairing positive and negative electrodes/electrolytes. [The theoretical cell capacity is calculated by  $C = C^+ / (1 + C^+ / C^-)$ ,<sup>4</sup> where  $C^+$  and  $C^-$  represent the theoretical capacity of positive electrode/electrolyte material and negative electrode material, respectively.  $C^+$  and  $C^-$  are scaled by Faraday's law to their individual active material. In VRF battery,  $VO_2^+$  and  $V_2(SO_4)_3$  are the active material for  $V^{4+}/V^{5+}$  and  $V^{2+}/V^{3+}$  redox couples, respectively. The specific energy is calculated as  $C \times$  cell voltage.]

### Electrochemistry:

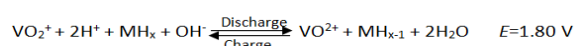
On the positive electrode in acidic environment



On the negative electrode in alkaline environment



The overall cell reaction is



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This research is supported by Research Grants Council of Hong Kong (GRF HKU 700209P and GRF HKU 700210P), University of Hong Kong SRT, The University Development Fund on the Initiative of Clean Energy and Environment.