

THE DEVELOPMENT OF FLOW BATTERIES FROM PROOF OF CONCEPT TO PILOT SCALE (AND BEYOND)

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ABSTRACT

Flow batteries have been suggested for applications such as the integration of renewable energy technologies, stand-by power, and as a tool for improving power transmission/distribution in electricity networks. A large number of chemistries have been identified, some of which are under commercial development, while others have only been characterized on a small laboratory scale or are impractical. The chemical and engineering challenges associated with developing a flow battery from proof of concept to a commercial system are discussed. Performance data from chemistries currently being developed at the University of Southampton will be used to provide specific examples of flow battery operation and development.

Keywords: flow battery, lead-acid, all-vanadium, zinc-air, zinc-cerium

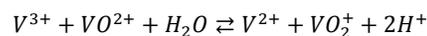
INTRODUCTION

Successful development of a flow battery involves overcoming both chemical and engineering challenges. At the proof of concept stage, chemistry dictates progress with reversible, efficient electron transfer and compatibility between electrolyte components being paramount. Scaling up towards commercially viable systems, engineering plays a larger role, with stack design optimization and system costs defining success. This paper outlines some of the critical parameters and challenges involved in this process and uses case studies from systems being developed at Southampton University to provide illustrative data.

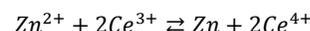
Chemistries

The selection of active species for the positive and negative electrode reactions influences system choices such as electrode material, electrolyte composition, membrane material, and cell design. Various categories of flow battery can be envisaged, determined by the electrode reactions. Examples of possible systems include:

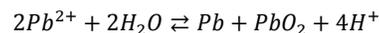
All-vanadium – Classical, membrane-divided redox flow battery utilizing active species that remain solvated during charge and discharge cycling.



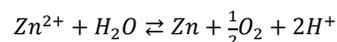
Zinc-cerium – Half redox flow battery and half metal flow battery. Membrane divided. Cerium ions remain solvated during charge/discharge cycling, whereas a phase change is required at the negative electrode, where metallic zinc is deposited during charging.



Soluble lead – Metal, metal oxide flow battery that does not require a membrane as a single active species, Pb^{2+} , is present in the electrolyte and both electrode reactions involve depositing solid phases during charging.



Zinc-air – Half metal flow battery, half unitized fuel cell. The negative electrode reaction involves a phase change between solvated Zn^{2+} ions and metallic zinc. The positive electrode is air breathing and similar to a polymer electrolyte membrane (PEM) fuel cell, where a catalyst system is required for oxygen evolution and reduction during charge and discharge respectively.



Case Study: Soluble Lead

A flow battery based on the two redox couples Pb/Pb^{2+} and $\text{Pb}^{2+}/\text{PbO}_2$ and a single electrolyte consisting of a high concentration of lead methanesulfonate in methanesulfonic acid has been developed from fundamental chemistry (voltammetric studies at a rotating disc electrode) to a pilot-scale flow reactor (bipolar stack with five 1000-cm² electrodes) (see Figure 1). This system has the advantage that no membrane is necessary but it does require the controlled deposition and dissolution of solid phases on both electrodes. The battery has an open circuit potential of ~1.8 volts (V) and can have an energy efficiency >70% and a cycle life exceeding 100 deep charge/discharge cycles. The power density on discharge peaks at approximately 1.2 V, which corresponds to 160 mW cm⁻² (see Figure 2).



Fig. 1. Pilot-scale flow reactor.

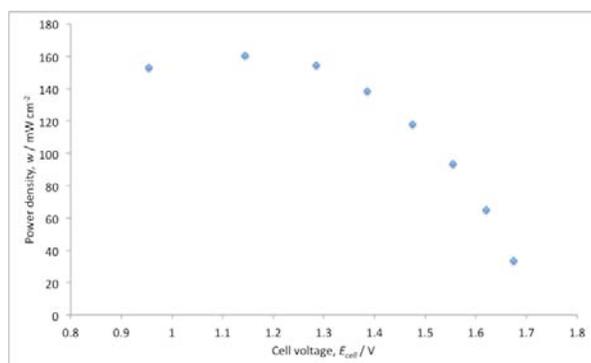


Fig. 2. Power density on discharge.

Successful mitigation of battery failure modes was required during scale-up from laboratory cell to pilot rig. Possible failure processes associated with the cell chemistry have been defined; lead (Pb) dendrites, lead dioxide (PbO_2) creep, and PbO_2 sludging. All

three processes result in electrical shorting between the positive and negative electrodes. Dendritic Pb growths typically occur during high-current charging. PbO_2 creep refers to solid, well-adhered PbO_2 deposits growing over the polymer cell components, eventually bridging the inter-electrode gap. PbO_2 sludging refers to amorphous, gel-like deposits forming from debris removed from the positive electrode. These deposits build up in areas of low electrolyte flow and through sedimentation onto horizontal cell components, such as electrode spacers and inlet manifolds. Optimizing mass transport through the flow chamber (cell design) and the use of selected electrolyte additives minimizes these failure modes.

REFERENCES

- [1] R.G.A. Wills and F.C. Walsh, Flow batteries, in *Encyclopedia of Electrochemical Power Sources*, 2010, Elsevier: Amsterdam., pp. 745-749.
- [2] R.G.A. Wills et al., "Developments in the soluble lead-acid flow battery," *J. Appl. Electrochem.* **40**, 2010, pp. 955-965.
- [3] M.J. Watt-Smith, R.G.A. Wills, and F.C. Walsh, Secondary batteries - flow systems, in *Encyclopedia of Electrochemical Power Sources*, 2010, Elsevier: Amsterdam., pp. 438-443.
- [4] A.A. Shah et al., "A Mathematical Model for the Soluble Lead-Acid Flow Battery," *J. Electrochem. Soc.* **157**(5), 2010, pp. A589-A599.
- [5] D. Pletcher et al., "A novel flow battery - A lead acid battery based on an electrolyte with soluble lead(II). Part VI. Studies of the lead dioxide positive electrode," *J. Power Sources*, **180**, 2008, pp. 630-634.
- [6] D. Pletcher et al., "A novel flow battery - a lead acid battery based on an electrolyte with soluble lead(II). V. Studies of the lead negative electrode," *J. Power Sources*, **180**, 2008, pp. 621-629.
- [7] D. Pletcher and R.G.A. Wills, "A novel flow battery - A lead acid battery based on an electrolyte with soluble lead(II). III. The influence of conditions on battery performance," *J. Power Sources*, **149**, 2005, pp. 96-102.
- [8] A. Hazza, D. Pletcher, and R.G.A. Wills, "A novel flow battery - A lead acid battery based on an electrolyte with soluble lead(II). IV. The influence of additives," *J. Power Sources*, **149**, 2005, pp. 103-111.

[9] D. Pletcher and R.G.A. Wills, "A novel flow battery: A lead acid battery based on an electrolyte with soluble lead(II). Part (II). flow cell studies," *Phys. Chem. Chem. Phys.* **6**, 2004, pp. 1779-1785.

[10] A. Hazza, D. Pletcher, and R.G.A. Wills, "A novel flow battery: A lead acid battery based on an electrolyte with soluble lead(II). Part I. Preliminary studies," *Phys. Chem. Chem. Phys.* **6**, 2004, pp. 1773-1778.

[11] P.A. Leung, C. Ponce-de-Leon, C.T.J. Low, A.A. Shah, and F.C. Walsh, "Characterization of a zinc-cerium flow battery," *J. Power Sources* **196(11)**, 2011, pp. 5174-5185.

[12] A.A. Shah, R. Tangirala, R. Singh, R.G.A. Wills, and F.C. Walsh, "A dynamic unit cell model for the all-vanadium flow battery," *J. Electrochem. Soc.* **158(6)**, 2011, pp. A671-A677.

BIOGRAPHICAL NOTE

Conference presenter: Dr Richard Wills is a senior research fellow with the Research Institute for Industry (RIFI) at the University of Southampton, UK. His research is focused on energy conversion technologies, in particular redox flow batteries, fuel cells, and electrode materials. He obtained a Ph.D. in Electrochemistry in 2004 working on a novel lead-acid flow battery. He then worked as a consulting engineer on a range of chemical, electrochemical, and energy storage projects until 2007. Between 2007 and 2008 he worked for Atraverda as a battery specialist developing ceramic and composite electrode materials before returning to RIFI in 2008 to further research the areas of batteries and electrochemical devices. He received the Dave Rice award in 2007 for research on lead-acid batteries.

