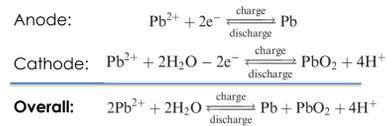


GRIDS Soluble Lead Flow Battery Technology

General Atomics and the University of California, San Diego
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OVERVIEW



Cell Potential = **1.76V**
 Energy Density = **75Wh/kg, 95Wh/L**

General Atomics (GA) and the University of California, San Diego (UCSD) are jointly developing a soluble lead flow battery¹ where the active lead material is dissolved into methanesulfonic acid, which allows for the use of a single electrolyte and eliminates the need for the separator or membrane material, greatly simplifying system design and cost.

Target

- Scalable design
- <\$100/kWh
- >3000 cycles

Advantages

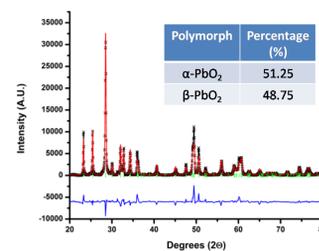
- Inexpensive active lead material dissolved in sulfonic acid
- Highly robust and reversible electrochemistry
- One reservoir without membrane/separator

Technology Impact

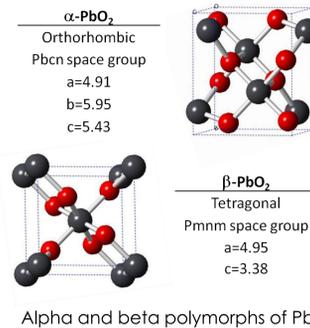
- Reductions in cost
- Extended cycle life
- Critical enabler for diverse distributed generation sources

1. Hazza, A., Fletcher, D., Wills, R., Phys. Chem. Chem. Phys., 6,1773–1778, 2004

TECHNICAL CHALLENGES



XRD spectra for PbO₂ including Rietveld refinement for α / β ratio



Alpha and beta polymorphs of PbO₂

PbO₂ Polymorphism: Lead-dioxide is known to occur in two polymorphs; an alpha phase taking the orthorhombic crystal structure, and the beta phase, a tetragonal structure. As the crystal structures have different physical properties, controlling which phase is deposited is important to flow battery performance and lifetime.

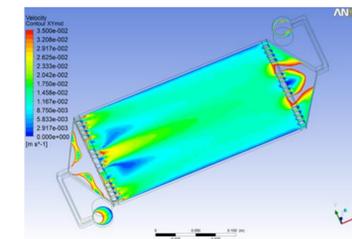
Deposit Reversibility: The reversibility of the deposited PbO₂ material has been identified as the major limiting factor for the soluble lead flow battery. As the number of cycles increases, the amount of PbO₂ that remains on the cathode also increases, depleting the electrolyte of Pb²⁺ ions available for subsequent charging of the cell. Over time, the energy storage capacity of the cell is diminished.

Dendrites: Deposited lead can grow long dendrites that are capable of shorting a cell in a bipolar stack architecture. As the number of cycles increases, the growth can become enhanced, leading to cell failure.

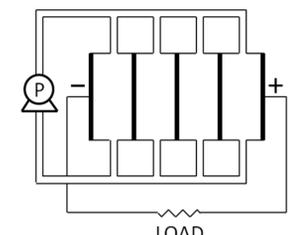
MODELING

ANSYS FLUENT: Fluid dynamic modeling ensures rapid iterative improvements in fluid uniformity. Additional testing and modeling enables refinement of mass transport and full utilization of active surface area for electrochemical reactions.

MATLAB: Conductive pathways and fluid flows (from ANSYS) can be combined into an overall model using MATLAB software. This enables improvements in cell geometry, materials optimization, and quantifies parasitic losses, for example: shunt (bypass) currents.



Computational Fluid Dynamics (CFD) of a reaction flow chamber



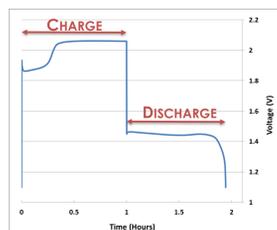
Simple model of a bipolar stack with cells in electrical series and fluidic parallel

Ab-initio: A potentially powerful method of analyzing and improving the electrochemical processes that occur at the interface,² is the *ab-initio* computational technique. These simulations are quantum mechanical in nature, begin from first principle calculations, and are ideally suited to addressing ion transport properties. For this research program, the *ab-initio* method will be focused toward the issue of incomplete PbO₂ reversibility. Simulations will be performed to understand the local ionic environment and methods of catalyzing the cathode reaction of PbO₂.

2. Meng, Y.S., et al., Journal of the Electrochemical Society, 151(8) A1134, 2004

RESULTS

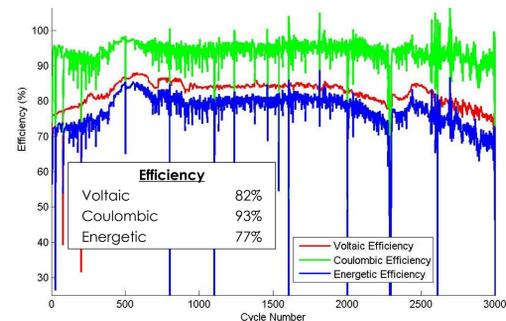
Small and medium sized soluble lead flow batteries have been built and tested. Long term deep-discharge cycling data show promising results and the ability to scale.



Example cycle behavior



Experimental setup for a soluble bipolar flow battery

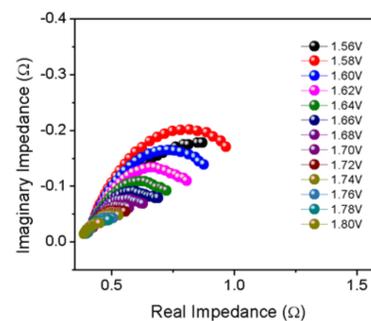


Efficiency values of a soluble lead flow cell over 3000 cycles

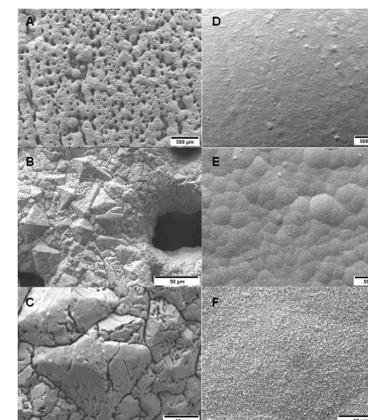
CHARACTERIZATION

Analytical Techniques: Research relating to the electrode and electrolyte is supported by a number of analytical electrochemical and characterization methods. This methods include cyclic-voltammetry (C-V), rotating disc electrode (RDE), electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), x-ray diffraction (XRD), and X-Ray Photoelectron Spectroscopy (XPS).

New Methods: An ex-situ and in-situ method for probing the deposit structure using X-ray Absorption Spectroscopy (XAS) will be performed to further understand the mechanism for the PbO₂ phases.



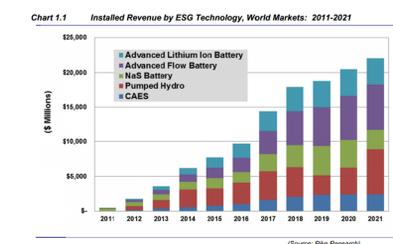
EIS at selected voltages to determine the charge transfer properties



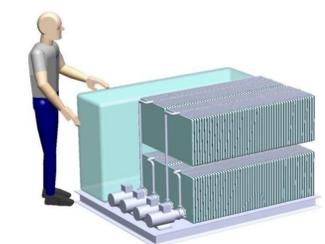
SEM images of PbO₂ cathode deposits at high (A-C) and low temperatures (D-F)

FLOW BATTERY OUTLOOK

- General Atomics and the University of California, San Diego have demonstrated the separator-free soluble lead acid chemistry and scaled to larger format bipolar cells.
- Deposit morphology and irreversibility can lead to reduced capacity and requires careful engineering to minimize system losses with extended cycling.
- The chemistry has proven robust and able to operate for over 3000 cycles.
- The grid energy storage market is estimated to be over \$20 Billion by 2020, with flow battery technology accounting for 25%.³
- The soluble lead acid flow battery offers a low cost, earth abundant material, and safe technology. It is an efficient and durable solution that can meet the growing need for grid scale energy storage.



Energy Storage Growth Forecast



Notional 20kW system

3. Dehamma, A., Bloom, E., Energy Storage on the Grid, Pike Research, 3Q 2011