

Identifying and Suppressing Side Reactions in Soluble Lead Flow Batteries to Achieve High Efficiency and Cyclability

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Flow batteries have been gathering significant momentum for use in large-scale energy storage applications. A major reason for this is their modular design, which separates energy and power components, enabling relatively easy and inexpensive methods to scale up. Several flow battery chemistries have been considered to be promising candidates, such as vanadium redox, polysulfide-bromine, and zinc-halogen. Soluble-lead chemistry has not been as well accepted, however, due to its relatively low energy efficiencies (~65%), low cycle life (~100-150), and low operating current densities ($20\text{mA}\cdot\text{cm}^{-2}$) [1]. Despite the challenges, overcoming these deficiencies is attractive because its materials costs are extremely low – a 20kW/20kWh system costs less than \$130/kW and \$45/kWh. Lead supply chains have also been historically well established, which makes potential manufacturing even easier and more cost effective. The fact that lead is the most highly recycled metal in the US is testament to the scale and efficiency of its use [2].

Soluble lead flow battery chemistry is distinct from classic lead-acid batteries. The anode and cathode of conventional lead-acid batteries are made of lead (Pb) and lead (IV) oxide (PbO_2), respectively. Upon charge, lead in both anode and cathode dissociates into lead (II) ions (Pb^{2+}), which then go on to form lead sulfate by reaction with electrolyte. This multi-phase reaction is simplified in the flow battery design by continuously pumping a solution containing Pb^{2+} and methanesulfonic acid (a greener analogue to sulfuric acid) between two carbon electrodes. Upon charge, Pb^{2+} deposits directly to Pb and PbO_2 on the anode and cathode, respectively. Upon subsequent discharge, Pb and PbO_2 are dissolved back into solution, in the form of Pb^{2+} (Figure 1). No separator is required.

The manner in which Pb and PbO_2 are deposited onto each electrode is critical. Sufficiently fast and homogenous flow is required to prevent local diffusion limitations, which would otherwise form Pb dendrites and large PbO_2 morphologies. Dendrite formation is detrimental due to potential shorting, while small nanoscale PbO_2 formation is necessary to promote efficient dissolution upon discharge. These factors are generally indicated by the charging potential; high overpotentials promote nucleation over growth, and therefore, densely packed films of nanoscale morphology. Conditions to promote relatively high charging overpotentials result in much more efficient dissolution. We showed that in such cases, using current densities of $20\text{mA}\cdot\text{cm}^{-2}$ we could achieve 2,000 cycles at an average ~80% energy efficiency [3].

A stable charging potential is notoriously difficult to control, however, due to a low voltage moiety present in all charge cycles following the first. The equilibrium full-cell charging potential is 1.46V, but at $20\text{mA}\cdot\text{cm}^{-2}$, the operating voltage is 2.01V. After the 1st cycle, an initial plateau 150mV lower constitutes ~10% of the profile. Extension of this plateau upon cycling leads to further potential drop – a good thing for voltaic

efficiency, but terrible one for Coulombic and overall energy efficiency. Half-cell measurements show that these low voltage features arise from the $\text{Pb}^{2+}/\text{PbO}_2$ redox couple, at the positive electrode. Beyond that, its origin is largely unknown and has been up for debate. Some propose it may be due to the presence of partially reduced PbO_x ($2 \leq x \leq 1$) species, while others suggest it is due to a higher surface area electrode, following the 1st discharge [4]. In either case, little evidence and mostly speculation exists.

Here we present the systematic study of materials deposited at the positive electrode at different states of charge – during the 1st and 2nd cycles. We show that both changes in surface morphology and the formation of chemical species not described by the theoretical reaction formula occur during the 1st discharge and 2nd charge, which account for variations in the cycling potential. Our conclusions were drawn from scanning and transmission electron microscopy (SEM & TEM), x-ray diffraction (XRD), x-ray photoelectron microscopy (XPS), and x-ray absorption spectroscopy (XANES & EXAFS). By doing so, we have expanded upon the reaction mechanism occurring in the soluble lead flow battery, and gained insight into how to enable even greater cyclability.

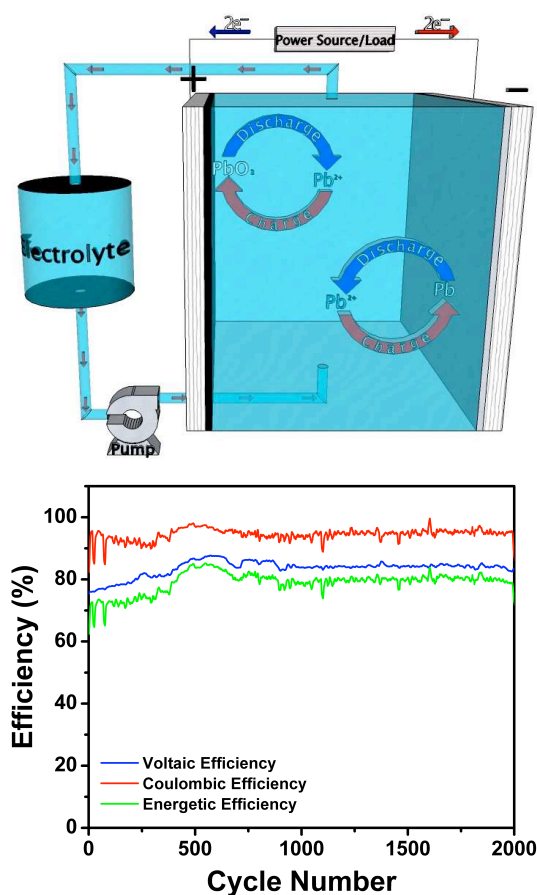


Figure 1. Schematic of soluble lead flow battery (top), and cyclability described in text (bottom).

References.

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