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An analytical study of a lead-acid flow battery as an energy storage system

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HIGHLIGHTS

- 2D lead-acid flow battery simulation which gives valuable mechanisms including electrochemical and surface reactions.
- Simulations successfully show surface concentrations of PbO and PbO_2 on the positive electrode.
- Simulations have shown that velocity is an important aspect when investigating lead deposition onto the electrodes.
- Effects of cell temperature, applied current density, initial species concentration, and external voltage were studied.

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ABSTRACT

The most important issue with our current clean energy technology is the dependence on environmental conditions to produce power. To solve this problem a wide range of energy storage devices are being explored for grid-scale energy storage including soluble lead-acid flow batteries. Flow batteries offer a unique solution to grid-scale energy storage because of their electrolyte tanks which allow easy scaling of storage capacity. This study seeks to further understand the mechanisms of a soluble lead acid flow battery using simulations. The effects of varies changes to operating conditions and the system configuration can be explored through simulations. The simulations preformed are 2D and include the positive electrode, negative electrode, and the flow space between them. Simulations presented in this study show Pb(II) surface concentration, external electric potential, and PbO/PbO_2 surface concentration on the positive electrode. Simulations have shown increasing cell temperature can increase external electric potential by as much as 0.2 V during charge. Simulations have also shown electrolyte velocity is an important aspect when investigating lead deposition onto the electrodes. Experimental work was performed to validate simulation results of current density and voltage. Good correlation was found between experimental work and simulation results.

1. Introduction

Why do we need energy storage? Political instability in oil-rich countries makes it risky for the U.S. to continue its reliance on petroleum. Furthermore, the use of fossil fuels for heat and power contributes to environmental pollution and global warming. There is no single solution to the pending energy crisis. A combination of solutions (solar, wind, biomass, hydrogen, and/or fuel cells) will be required to meet our future energy needs. This is because the output of renewable sources varies by environmental conditions. For example, the range of output from solar power and wind power generation depends on the weather. Grid-scale energy storage that is efficient and competitive in pricing remains a missing piece of the renewable energy puzzle.

Lead-acid flow batteries are a promising technology for grid-scale energy storage. Flow batteries can be easily scaled to fit any system requirements making them optimal for load leveling. When energy storage must be increased, all that needs to be changed is the capacity of the electrolyte storage tanks. Lead-acid flow batteries offer a high energy density and cell voltage when compared to vanadium or zinc flow batteries. The cost of producing a lead-acid battery is much lower than most flow batteries as the electrolyte is easily obtained and no proton exchange membrane is required.

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Nomenclature

c_i	species concentration [mol m^{-3}]
cO_i	initial concentration [mol m^{-3}]
cs_i	surface concentration [mol m^{-3}]
D_i	diffusivity coefficient [m^2 s^{-1}]
E_{eq}	equilibrium potential [V]
$E_{0,eq}$	ambient equilibrium potential [V]
E_{pos}	equilibrium potential at positive electrode [V]
F	Faraday's constant [C mol^{-1}]
i_{app}	applied current density [A m^{-2}]
i_{cycle}	current density per cycle [A m^{-2}]
i_{dl}	current density at the electrode surface [A m^{-2}]
$\boldsymbol{i}_l$	local current density [A m^{-2}]
$\boldsymbol{i}_s$	source current density [A m^{-2}]
$i_{loc,m}$	local current density per unit mass [A (m^{-2} kg^{-1})]
i_{total}	total current density [A m^{-2}]
i_0	open circuit current density [A m^{-2}]
kOb_i	backward rate constant [m^4 (s^{-1} mol^{-1})]
kOf_i	forward reaction rate constant [m^4 (s^{-1} mol^{-1})]
kO_i	rate constant [m s^{-1}]
$\boldsymbol{l}$	length of the section [m]
L_{entr}	laminar flow entrance length [m]
$\boldsymbol{n}$	normal vector
$\boldsymbol{N_i}$	concentration flux [mol (m^{-3} s^{-1})]
n_m	number of participating electrons
p_i	pressure [Pa]
p_{entr}	laminar entrance pressure [Pa]
phil	electrolyte potential [V]
phisext	external electric potential [V]
Q_l	heat flux [W m^{-2}]
Q_s	power dissipation [W]
R	universal gas constant [J (mol^{-1} K^{-1})]
$R_{i,src}$	reaction rate
$R_{i,tot}$	total rate expression
$R_{i,m}$	local rate expression
$R_{s,i}$	surface rate expression
T	fluid temperature [K]
T_{ref}	reference temperature [K]
$tfluxy_i$	total flux in y-direction [mol (m^{-2} s^{-1})]
u_i	boundary flow velocity [m s^{-1}]
$\boldsymbol{u}_{m,i}$	flow velocity [m s^{-1}]
z_i	valance/charge number
α_a	anode stoichiometric coefficient
α_c	cathode stoichiometric coefficient
ρ	density [kg m^{-3}]
$\varnothing_s$	electrode electric potential [V]
$\varnothing_l$	electrolyte electric potential [V]
$\sigma_{i,s}$	site occupancy number
μ	dynamic viscosity [Pa s]
$\nu_{i,m}$	stoichiometric coefficient
θ_i	fraction of free sites
Γ_s	density of sites [mol m^{-2}]

The biggest challenge in lead-acid flow battery technology is lead deposition on the electrodes. Overtime the process of deposition and removal degrades the electrode efficiency reducing the performance of the flow battery. Life cycle is very important to grid-scale energy storage. Reduction in efficiency and replacing electrodes costs money in materials, training, and service. Several solutions to the problem of lead deposition have been explored; however, none offer a solution that allows for an extended life time. Very few analytical studies have been done on the soluble lead-acid flow battery. Experimental work was performed to validate simulation results.

Gu, Nguyen, and White developed a mathematical model of a lead acid cell [1]. They based their mathematical model on the assumption that the cell geometry and structure can be considered as one uniform macroscopic unit with charge transfer and other transport effects taking place normal to the longitudinal direction [1]. Gu et al. showed that the exchange current density is dependent on the working temperature [1]. Also, the cell geometry affects the output; a thin positive electrode influences the output voltage more than a thick one. The authors attributed this to a greater degree of polarization in the thin positive electrode. Porosity also has a strong influence on the cell as electrodes having greater porosity have greater discharge times [1].

Mauracher and Karden used impedance spectroscopy to study the dynamic model of lead acid batteries [2]. Their study was based on the principle that phenomenological models requiring several parameters seldom sufficiently predict the different conditions of the cell. Instead they based their model on the physicochemical elements of the cell. The differential equations for the working of the cell were developed considering a stationary electrolyte and then solved and the solutions were considered equivalent to an electric circuit. The model was developed based on Randles equivalent circuit and then an equilibrium voltage was obtained in the case of no current. The authors were able to find out the concentration overvoltage values based on the state of charge and input current [2].

Simulation along with experimental verification of the lead acid battery system was done by Achaibou et al. [3]. They developed their model considering that active parts of both anode and cathode convert to lead sulfate during discharge and charging results in liberation of sulfate ions and thereby causes an increase in electrolyte concentration. Based on the voltages obtained and the currents applied the authors showed that voltages varied linearly with time for different applied currents at 25 °C. The authors were able to correlate similar results from the experimental study of a lead acid battery. Root mean square error values showed that the model fits closely with experimental results. Errors in the model were attributed to the specificity of the experimental conditions with respect to the model which was deemed to be more generic [3].

Shah et al. developed a transient, analytical model for an all vanadium flow battery and compared it to experimental results [4]. The analytical model considers mass transport, charge transport, electrode surface reactions, and electrochemical effects [4]. It is a 2D model with a domain that includes two electrodes, two reservoirs, and an electrolyte membrane. Mass balance controls charged species concentrations in the electrolyte and on the electrode surface. Charged species transport includes diffusion, migration, and convection. The electrolyte is treated as incompressible and as a dilute-solution with water being the dominant component [4]. The thickness of deposited layers on the electrodes is assumed small compared to the inner electrode gap. This is a good approximation at low cycle numbers; however, the thickness of the electrodeposited layers has an increased effect as cycle numbers increase [4]. The system is assumed isothermal. Shah et al. report the simulation results have a good degree of accuracy in reporting trends based on experimental data [4].

Shah et al. developed a transient model for a lead-acid flow battery incorporating mass transport, charge transport, and