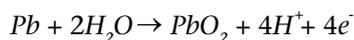


Modeling Positive Plate Corrosion in Lead–Acid Batteries

by Vijayasekaran Boovaragavan

Lead-acid battery technology is the oldest and still a successful secondary battery technology for many applications such as uninterruptible power supplies and automobile SLI (starting, lighting, and ignition). One of the factors that limit the cycle life of this battery technology is the corrosion process that is taking place between the positive grid material and the positive active material at about 50 to 350 mV close to the open-circuit potential of the positive plate. Corrosion leads to a passive layer formation between the grid and the active mass. This phenomenon is also called premature capacity loss. The positive grid material is a pure lead, Pb, or an alloy with antimony, Pb-Sb and the positive active material is the lead-dioxide, PbO₂. The electrochemical reaction that causes this corrosion process can be expressed as:



It is important to mention that the lead, Pb in this reaction, is coming from the grid material and it is different from the spongy lead material, Pb that is used as negative active material in the negative electrode. This reaction not only decreases the positive grid conductivity but also consumes water. The performances of both the flooded and valve-regulated lead-acid battery designs are affected by this corrosion process. Thus, it is important to qualitatively represent this mechanism using a mathematical model. This effort has been attempted in this work.

Three different modeling approaches are used to incorporate the effect of corrosion in the first-principles based porous electrode model of a lead-acid cell. These approaches are used to examine the effects of corrosion during discharge, rest and charge processes. First, the electronic conductivity of the positive plate is empirically expressed as a function of \bar{N} , the number of cycle. Next, a current-resistance loss term is considered to account for the increase in electronic resistance due to the formation and growth of passive corrosion layer. Finally, the corrosion phenomenon is incorporated as a side reaction that is taking place in the positive plate. The continuum model for the lead-acid battery was derived based on concentrated solution theory, porous electrode theory, modified Ohm's law and other transport and kinetic phenomena. Unlike Ni or Li systems, lead-acid battery has significant porosity variations as a

function of time and distance across the thicknesses of porous electrodes due to sulfate formation at porous electrodes. It was found from the further investigation that the model with corrosion mechanism incorporated as a side reaction might be suitable for studying the effects of corrosion on the cycling performances of a lead-acid cell. A detailed explanation on this conclusion and the derivation of the continuum model can be found elsewhere.¹⁻²

Typically, the cycle life of a portable lead-acid battery is between 200 and 400 cycles during low to moderate rates of operations. Figure 1 shows the effect of corrosion on the electrochemical performances of the lead-acid cell as a function of cycle numbers at high rates of charge and discharge. It can be seen that a significant loss in capacity, which is close to the end of life capacity, is noticed due to the decreased grid conductivity at the positive plate within first 25 cycles of charge and discharge. The model is capable of quantifying the effects of corrosion on the electrochemical performances. Thus, the model developed with the fellowship support will be a very useful tool to investigate the methods that can possibly mitigate this degradation effects.

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About the Author

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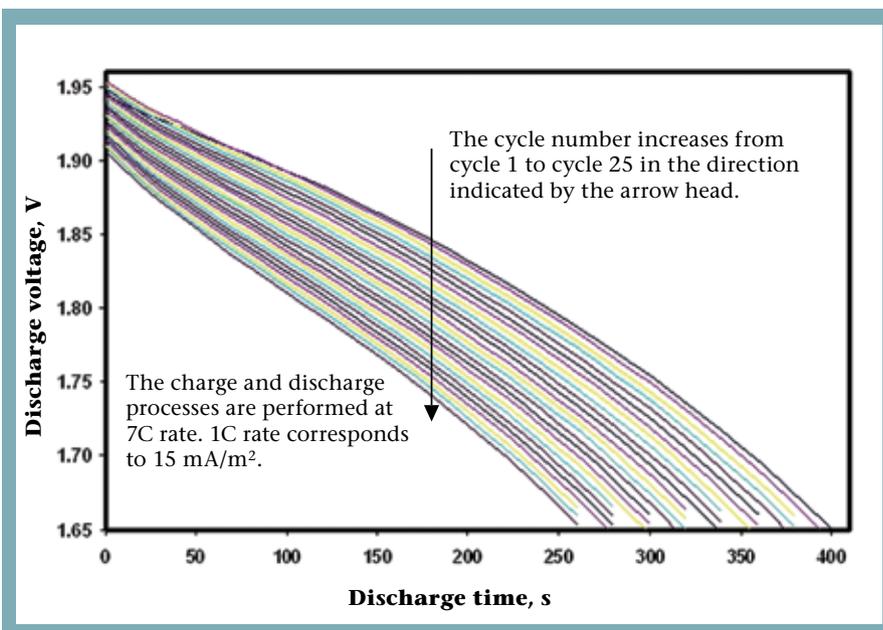


Fig. 1. Effect of corrosion on the cycling performance of a lead-acid cell.