Modeling Corrosion in Lead-Acid Cell and Parameter Extraction from Lithium-Ion Cells

by Vijayasekaran Boovaragavan

Secondary batteries are widely used in portable consumer devices, uninterruptible power supplies, tools, and as automobile starters with emerging applications in hybrid electric vehicles and electric vehicles to improve cost effectiveness, reduce weight, and increase lifetime. Modeling of these batteries, which include lead-acid, lithium-ion, and nickel-metal-hydride systems has gained momentum to simulate process (voltage, power, energy, etc.,) and intrinsic variables (solid-phase concentration, electrolyte potential, local current density, etc.,). However, there are still some processes, such as corrosion of positive plate in lead-acid batteries and capacity fade mechanism in lithium-ion batteries that force limitations to promote secondary batteries for emerging technologies. Results from tasks on modeling corrosion in lead-acid cells and previously proposed tasks on extraction of lithium-ion cell parameters, which are part of both the current and past Fellowship work, are reported.

The rigorous continuum battery models are derived based on concentrated solution theory, porous electrode theory, modified Ohm's law, and other transport and kinetic phenomena.[1-2] They consist of four regions as shown in Fig. 1 and usually have multiple partial differential equations in multiple domains to solve for process and intrinsic variables.[3] The limiting factor for cycling efficiency of a lead-acid cell is the corrosion mechanism depicted between the plate gird material and positive active mass in PbO_2 electrode (shown in Fig. 1). Thus, corrosion prevention in PbO_2 electrodes can greatly help improve performance and cycle life. However, modeling the corrosion mechanism in a lead-acid cell has not been addressed in detail in the literature. In this work, different approaches are followed to model the corrosion mechanism. These approaches are based on using a modified Butler-Volmer rate expression for the positive plate kinetics during charge, rest, and discharge. First, the corrosion mechanism is incorporated as a side reaction in PbO_2 electrode kinetics; next an I-R loss term is included to account for the increase in electronic resistance due to formation and growth of the corrosion layer; and finally the electronic conductivity of the PbO_2 electrode is empirically expressed as a function of N, the number of cycles. The rigorous model for lead-acid batteries has been solved with the new kinetic expressions using

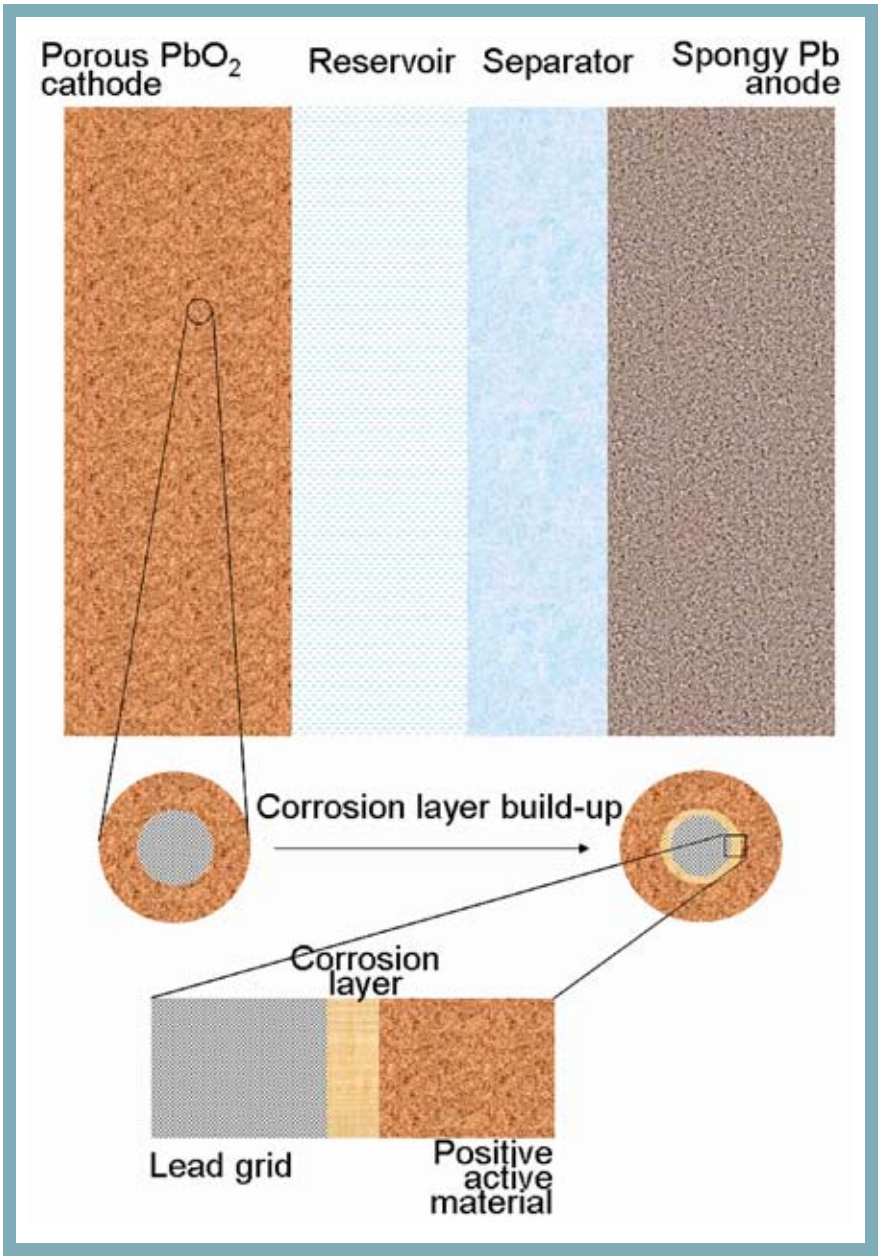

Fig. 1. *Schematic of a flooded lead-acid cell with corrosion layer formation.*

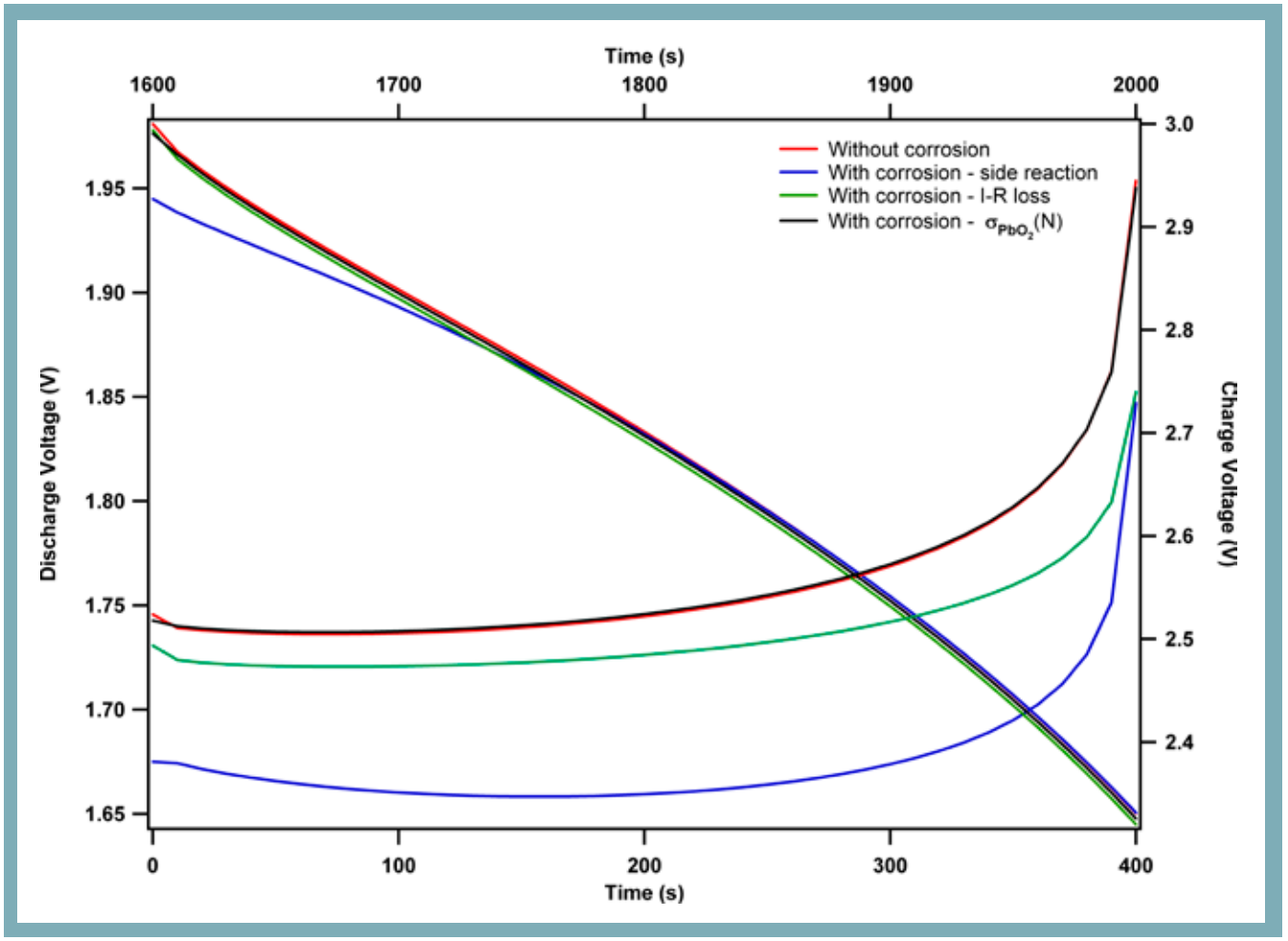

Fig. 2. *Comparison of charge and discharge profiles between models with and without corrosion mechanism.*

finite differences in *x*-direction and compared with the same model without addressing the corrosion mechanism. Figure 2 shows a comparison between charge and discharge profiles from the model with and without corrosion. With this modeling capability, it is identified that the models can now be used to study the effect of corrosion on cycling. Further, it can also be used to extend battery cycle life by optimizing the electrode design.

An efficient reformulated rigorous model for lithium-ion batteries was reported by the author.[4] This efficient reformulated model has now been successfully used to extract parameters for lithium-ion batteries and the results have been published elsewhere.[5] The rigorous model takes 1-3 minutes to run and is not ideal for use in hybrid systems and on-line control. The reformulated model only takes less than a second for extracting three parameters and works as good as the rigorous model predictions without loss of accuracy. This approach works for low rates of discharge. Currently, work is underway to enable this for high rates of discharge and to study the effect of corrosion in PbO_2 electrodes used in lead-acid batteries.

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