Study of Charge Kinetics in Valve-Regulated Lead-Acid Cells
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Current consumer applications of valve-regulated lead-acid (VRLA) batteries range from powering bicycle headlights to powering electric vehicles. Since the valve-regulated design for lead-acid batteries is relatively new, fundamental understanding of charging mechanisms is lacking. Since the earliest published models of the lead-acid cell, 1,2 extensions have been proposed, 3,4 with a more recent advancement being a two-dimensional model including free convection. 6 Still lacking, however, is an accurate description of charge. The model here is an improvement to the one presented in Ref. 5 and employs more detailed reaction mechanisms and fewer adjustable parameters to obtain more satisfactory comparisons to experimental results. In this work we compare mathematical model predictions of half-cell voltages, current, and gassing behavior to experimental results of VRLA cells in order to help us understand charging behavior.

The above figure shows model and experimental half-cell voltages during charge of a 19-plate cell with a constant 15-A current to a cell voltage lid of 2.5 V. The Pb electrode (b) exhibits a sharp voltage drop at 160 minutes, which results in termination of galvanostatic charge. The model results of the figure below can help us understand why the Pb electrode limits charge.

We use the widely accepted dissolution-transport mechanism: the three-step, sequential process of (i) PbSO₄ dissolution into lead ions, (ii) liquid-phase lead ion transport, and (iii) electrochemical reduction of lead ions to Pb to derive the model’s electrochemical kinetic expressions. The above figure gives the fractional limiting current, within the Pb electrode, and shows that galvanostatic charge represents an approach to limiting current conditions; \( i_{\text{lim}} = \frac{1}{i_{\text{in}} + i_{\text{out}}} \rightarrow 1 \). Limiting current conditions are defined as the point at which the limitations of steps (i) and (ii) result in a zero concentration of lead ions at the Pb charging surface. The departure of lead ion concentration at the PbSO₄ particle surface from the equilibrium value is represented by \( \Delta c_{\text{p}} \) (dissolution). Similarly, \( \Delta c_{\text{i}} \) represents the difference in lead ion concentration between the PbSO₄ particle surface and the Pb charging surface (transport). At any point during charge, we can evaluate the relative importance of step (i) versus step (ii) by comparing \( \Delta c_{\text{p}} \) to \( \Delta c_{\text{i}} \). In the first 150 minutes of charge, limitations due to lead ion diffusion dominate over those of PbSO₄ dissolution; however, the effects of step (i) are not negligible. During this time period, the Pb half-cell voltage is nearly constant because the electrode is sufficiently far from limiting-current conditions and the current is relatively low.

After about 150 minutes, the Pb electrode polarizes more rapidly due to step (i). In other words, at this time the PbSO₄ particles have shrunk to the point that they can’t dissolve rapidly enough to avoid a significant depletion of lead ions in the electrode pores, and this limits charge.

Since the charging mechanism of the PbO₂ electrode has not been established, we at first tried to represent its behavior with a dissolution-transport mechanism. We were not successful; however, using the suggestion of Eckdunge and Simonsson of a two-step, solid-state electrochemical mechanism, we found the satisfactory agreement between the experimental PbO₂ half-cell voltage data and model predictions shown in the first figure (a).

The model also predicted the characteristic double-peak gas-flow behavior seen when charging VRLA cells with constant current to a specific voltage lid. The first peak is due to the onset of significant amounts of \( \text{O}_2 \) generation even though the internal residual gas is dominantly \( \text{H}_2 \). The second peak is due to the onset of \( \text{H}_2 \) evolution. Conditions under which to expect charging difficulties as well as improved charge regimes are also discussed.