



# Role of electrical resistance of electrodes in modeling of discharging and charging of flooded lead-acid batteries



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## HIGHLIGHTS

- Variation in resistance of electrodes included in mathematical model.
- Adopts reasoned expressions for changing area of active materials.
- Model predictions are as good as those obtained from non-mechanistic models used earlier.
- Points to the significance of conductivity in the charging of deep discharged electrodes.

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## ABSTRACT

Electrical resistance of both the electrodes of a lead-acid battery increases during discharge due to formation of lead sulfate, an insulator. Work of Metzendorf [1] shows that resistance increases sharply at about 65% conversion of active materials, and battery stops discharging once this critical conversion is reached. However, these aspects are not incorporated into existing mathematical models. Present work uses the results of Metzendorf [1], and develops a model that includes the effect of variable resistance. Further, it uses a reasonable expression to account for the decrease in active area during discharge instead of the empirical equations of previous work. The model's predictions are compared with observations of Cugnet et al. [2]. The model is as successful as the non-mechanistic models existing in literature. Inclusion of variation in resistance of electrodes in the model is important if one of the electrodes is a limiting reactant. If active materials are stoichiometrically balanced, resistance of electrodes can be very large at the end of discharge but has only a minor effect on charging of batteries. The model points to the significance of electrical conductivity of electrodes in the charging of deep discharged batteries.

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## 1. Introduction

Systematic use of mathematical models to predict performance of a lead-acid battery to meet a variety of purposes is the focus of many investigations [2–10], and extensive reviews of this work also exist [11,12]. Though differing in details, all models proposed so far take into account: (i) migration and diffusion of reactive species, (ii) ohmic resistance in the electrolyte, and (iii) the finite rate of charge transfer reactions. Resistance to electron conduction in the electrodes is also an important factor that needs attention. It is affected by changes in the porosity of the electrode, and existing models do take into account this aspect. However, electrical resistance of electrodes is also affected by another process. Active materials are

electron conductors while lead sulfate is an insulator. Thus, the resistance of an electrode changes as active materials react to form lead sulfate. This effect of change in chemical composition of an electrode on its resistance has so far not been accounted for in models. Resistance of an electrode varies sharply when a critical conversion of active materials is reached and the change can be dramatic. Measurements of Metzendorf [1] show that the conductivity of lead dioxide electrode is about  $100 \text{ S m}^{-1}$  at a conversion of 60% and that it drops by nearly five orders of magnitude when conversion increases by only about 5%. A similar effect was observed by Metzendorf [1] for lead electrode also when conversion increases from 70% to 75%. Metzendorf [1] used concepts of percolation theory to propose that path for electron conduction ceases to exist when the volume fraction of active material is lowered to a critical value, commonly known as the percolation

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threshold. Fraction of the initial amount of active material consumed upon reaching the percolation threshold will be referred to as critical fractional conversion. At the point of critical fractional conversion, electrode behaves like an insulator since a conducting path does not exist, and battery stops discharging. Metzendorf [1] suggests this to be the explanation for the well known difference between the theoretical capacity of an electrode,  $Q_{\text{theo}}$ , and its nominal capacity,  $Q_{\text{nom}}$ , i.e., the observed maximum capacity that it can deliver. All these effects of variation in the resistance of an electrode caused by change in its composition have been ignored in mathematical models so far, and are investigated here. In view of the percolative nature of electrical conductivity, the effect of changing resistance of an electrode will be important only when the critical fractional conversion of active materials is approached. This can occur only under deep discharge conditions, and when electrodes are the limiting reactants. When electrodes are the limiting reactants, a sharp decline in voltage (a 'knee') is observed towards the end of discharge. Successful modeling of this has not been possible without the use of empirical expressions. It will be shown that such non-mechanistic approaches can be avoided by introduction of effect of the composition of an electrode on its resistance and a justifiable expression for changes in the area of active materials.

## 2. Model equations

A one dimensional ( $x$ ) macro homogeneous model of a lead-acid battery is used here. As the set of equations employed is very similar to those of Gu et al. [5] and Cugnet et al. [2], only the differences will be discussed in detail.

### 2.1. Conductivity of electrodes

Metzendorf [1] treats the electrode as a porous medium where the solid itself is a physical mixture of non-porous particles of active material and lead sulfate. He uses the percolation model to derive the following expression for effective conductivity:

$$\sigma_{\text{eff}} = \sigma_o(1 - \varepsilon)^{0.5} \left[ \frac{1 - r - \frac{d_c}{(1 - \varepsilon_o)}}{(1 + (\Delta V)^* r) \left(1 - \frac{d_c}{(1 - \varepsilon_o)}\right)} \right]^{1.7} \quad (1)$$

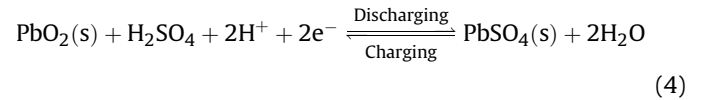
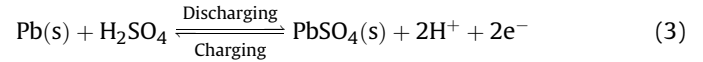
where  $\sigma$  is the conductivity, subscript eff refers to the effective value in a porous electrode, and subscript  $o$  stands for pure material.  $\varepsilon$  is the porosity of the electrode, and subscript  $o$  stands for the electrode in the pristine condition. The term  $(1 - \varepsilon)^{0.5}$  is the usual Bruggeman correction [13]. Further,  $r$  is the fraction of active material converted to lead sulfate,  $d_c$  is a packing parameter, and  $(\Delta V)^*$  is the ratio of the difference in the molar volume of lead sulfate and active material to the molar volume of the active material. Metzendorf [1] assumes lead particles to be ellipsoidal and lead dioxide particles to be spherical, and uses a different value of  $d_c$  for the two electrodes. As his assumptions of the particle shapes might not be valid for all preparations, the value of  $d_c$  for uniform sized spheres is used here in both the electrodes. As will be seen a little later, a modified form of the above expression is needed if the electrode also contains a non-conducting inert solid. The following expression is applicable for that case:

$$\sigma_{\text{eff}} = \sigma_o(1 - \varepsilon - \varepsilon_{\text{in}})^{0.5} \left[ \frac{x_o(1 - r) - \frac{d_c}{f_o}}{(1 + x_o(\Delta V)^* r) \left(x_o - \frac{d_c}{f_o}\right)} \right]^{1.7} \quad (2)$$

where  $\varepsilon_{\text{in}}$  is the volume fraction of the inert material,  $f_o = 1 - \varepsilon_o$  and  $x_o = 1 - \varepsilon_{\text{in}}/f_o$ . When the battery is in fully charged condition,  $d_c/f_o$  is less than  $x_o$  and hence conductivity decreases as  $r$  increases. Eq. (2) shows that conductivity goes to zero when fractional conversion reaches a critical value  $r_c = 1 - d_c/(f_o x_o)$ , and the electrode behaves like a perfect insulator. However, lead sulfate will also have some conductivity, and a very low conductivity of  $10^{-8} \text{ S m}^{-1}$  is assigned to electrodes when  $d_c/(f_o - \varepsilon_{\text{in}}) \geq 1 - r$ . Model predictions are insensitive to changing this number up or down by an order of magnitude.

### 2.2. Conservation of charge

Chemical reactions occurring in the battery at the negative and positive electrodes respectively are:



As lead sulfate is sparingly soluble in sulfuric acid, sulfate formed during discharge precipitates. Hence, the solid phase of the electrode is a physical mixture of two solids to which the theory of Metzendorf [1] can be applied. Charge conservation in the solid phase is given by

$$0 = \frac{\partial}{\partial x} \left( \sigma_{\text{eff}} \frac{\partial \phi_s}{\partial x} \right) - S \quad (5)$$

where  $\phi_s$  is the potential in the solid phase, and  $S$  is the rate of charge transfer reactions per unit volume. Charge conservation in the electrolyte phase is given by

$$0 = \frac{\partial}{\partial x} \left( \kappa_{\text{eff}} \frac{\partial \phi}{\partial x} \right) - \frac{RT}{F} \frac{\partial}{\partial x} \left( \kappa_{\text{eff}} \frac{1 - 2t_+}{C} \frac{\partial C}{\partial x} \right) + S \quad (6)$$

where  $\kappa_{\text{eff}}$  is the effective conductivity of the electrolyte in the porous electrode,  $F$  is Faraday's constant,  $\phi$  is the potential in the electrolyte,  $C$  is the concentration of the acid, and  $t_+$  is the transport number of protons.

#### 2.2.1. Battery reactions

Only the battery reactions given above occur during discharge while electrolysis of water can also occur during charging. Butler-Volmer equation is used to calculate the rate of the charge transfer due to battery reactions:

$$S_{\text{bat}} = a_o \mathcal{F} i_o^{\text{ref}} \left( \frac{C}{C_{\text{ref}}} \right)^\gamma \left[ e^{\frac{\alpha(\phi_s - \phi - E^*(C))F}{RT}} - e^{-\frac{\beta(\phi_s - \phi - E^*(C))F}{RT}} \right] \quad (7)$$

where  $i_o^{\text{ref}}$  is the exchange current density at the reference acid concentration,  $a_o$  is the area of the active material per unit volume in a fully charged electrode, and  $E^*(C)$  is the equilibrium potential at the local acid concentration,  $C$ .  $\mathcal{F}$  is a coverage factor, and will be discussed in detail in Section 2.3.

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