Modeling lead/acid batteries that have positive electrodes containing hollow, glass microspheres

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Abstract

This paper uses a computer model to predict the performance of positive electrodes containing hollow, glass microspheres. The model's performance prediction for these plates is then compared with experimental data. The model helps to make clearer the effect the glass microspheres have on plate performance. At medium to high specific rates, the positive plate performance is improved because a higher percentage of the plate's active material reacts with the electrolyte stored within the plate. At low specific rates, the performance is reduced because the conductivity of the plates with the microspheres, as characterized by the critical volume fraction, is lower.

Introduction

This paper resulted from our attempts to quantitatively explain results from tests previously conducted at the University of Idaho [1, 2]. In some of these tests [1], the addition of hollow, glass microspheres improved the positive active material utilization for medium to high specific discharge rates. This improvement was thought to result from a better ratio of electrolyte to positive active material. The performance increase, however, was not observed at the low specific rates. Subsequently, in other tests [2], the authors found that adding hollow, glass microspheres to the negative active material reduced that plate's low rate capacity performance. These negative plate results were consistent with the hypothesis suggested by Metzendorf [3] that the low-rate capacity of both the negative and positive plates was limited by the plate's conductivity. After a critical amount of active material, referred to as the critical volume fraction, is converted to lead sulfate during a discharge, the conductivity is sharply reduced and the reaction is stopped.

In order to investigate Metzendorf's hypothesis, the authors of this paper developed a conductivity model [4] for lead/acid battery electrodes. The model provided a reasonable comparison with the low-rate performance of the negative plates previously tested [2] and helped verify Metzendorf's hypothesis. Although the model compared favorably with the experimental data, it was restricted to constant-current discharges at low rates. A quantitative model that used a few fundamental, physical parameters to predict cell performance over a wide range of constant-current discharges was desired. In a companion paper [5], the conductivity model [4] previously developed was combined with diffusion models so that cell performance over a wide range of discharges could be predicted.

This paper compares experimental data [1] on positive plates containing different amounts of hollow, glass microspheres with simulated data generated by the combined

conductivity and diffusion computer model [2]. The experimental data are from plates containing paste with a weight ratio of glass microspheres to lead oxide of 2.2, 4.4, and 6.6%, respectively. The true density of the microspheres is about 0.2 g/cm^3 and the volume percentage of these microspheres in the paste range from about 20 to 50% (see Table 1). The next section discusses the parameters required by the model and provides those parameters for each type of positive plate tested.

Model parameters

The plate parameters needed by the model to simulate a constant-current discharge can be divided into conductivity parameters and diffusion parameters. Electrical resistance is one conductivity parameter the model requires. This parameter depends on the resistance of the grid, wire connections, size and length of cable, and other resistive terms associated with the experimental setup. The electrical resistance for each cell type is estimated from the experimental data [5]. A voltage correction, which accounts for variations in the initial electrolyte concentration, is also estimated. The electrical resistance and voltage correction are both provided in Table 1 for the different types of positive plates discussed in this paper.

The other conductivity parameter required by the model is the percent of active material that can be converted to lead sulfate before the paste becomes nonconductive. This percentage is called the critical volume fraction [3] and can be estimated from the conductivity model previously reported [4] when the volume percent of glass microspheres in the paste is known. For a paste with no glass microspheres, the critical volume fraction is about 60%. As the amount of glass microspheres in the paste increases, this fraction decreases. The critical volume fraction for the plates with the highest loading of glass microspheres, the 6.6% plates, is only 37%. Table 1 provides both the critical volume fraction and paste density for each plate type. As will be discussed later, the paste density is used by the model to find the distance into the plate where the reaction occurs.

TABLE 1

Plate parameters for the battery model

Plate type	Weight ratio of glass microspheres to lead dioxide		
	2.2%	4.4%	6.6%
Electrical resistance (Ω)	0.0383	0.05612	0.02333
Voltage correction, ΔV_i (V)	+0.0323	−0.0205	−0.0155
Volume % of microspheres in paste (%)	19.5	34.0	48.9
Critical volume fraction, V_c (%)	58.5	50.0	37.0
Paste density (g/cm^3)	2.53	2.09	1.75
Porosity percentage (%)	26.89	26.41	28.85
Plate diffusion coefficient, D_p (m^2/s)	9.5728^{-10}	9.4020^{-10}	1.0271^{-9}
Plate thickness (mm/in)	2.21/0.087	1.86/0.0772	1.96/0.0772

The diffusion coefficient, D, for the sulfate ions in the electrolyte is modeled as being constant (i.e., $D = 2.081^{-6}$ in^2/s or 3.56^{-9} m^2/s). The average diffusion coefficient for the electrolyte within the plate is found by correcting the ion diffusion coefficient between the plates by the porosity, ρ, and tortuosity, τ, of the plate. From this evaluation the plate's tortuosity was assumed to be one. The following equation, from Bode [6], shows how porosity determines the average diffusion constant within the plate:

$$D_p \approx D \frac{\rho}{\tau} \approx D\rho \tag{1}$$

The porosity and the plate diffusion coefficient for the different types of plates are given in Table 1.

A plate's porosity is also needed to establish the amount of electrolyte stored in the plate. The ions of the stored electrolyte are assumed to be available for reaction and do not need to diffuse to the reaction site. Even at very high rates, it is assumed that the ions within a plate will react to the same concentration as occurs at the reaction site. In Table 1, the average porosities and plate thicknesses for the different plate types are given. The plate thicknesses are needed to compute the electrolyte volume stored in the plates.

The five parameters required by the model to characterize the performance of these plates are given in Table 1. These parameters are the circuit resistance of the cell, the initial cell voltage correction, the critical volume fraction where the paste becomes nonconductive, the paste density, and the plate's porosity.

Two different equations are used to find the electrolyte concentration within a cell. A finite difference equation uses the diffusion constant to find the electrolyte concentration between the plates. The electrolyte concentration inside the plate is estimated with a second order MacLaurin series expansion. The first and second differentials associated with this series expansion are a function of the average plate diffusion constant, D_p. The MacLaurin series estimate the concentration within the plate as a function of the distance into the plate, x_p, as:

$$m(x_p) = m|_{x_p-0^+} + x_p \frac{\partial m}{\partial x_p}\bigg|_{x_p-0^+} + \frac{x_p^2}{2!} \frac{\partial^2 m}{\partial x_p^2}\bigg|_{x_p-0^+} + \ldots \tag{2}$$

where $m|_{x_p-0^+}$ is the concentration at the surface of the plate and is found from the finite difference equation. We will subsequently refer to the concentration at the plate's surface as m_B.

The values for the first and second partial derivatives can be found or estimated, see ref. 5 for the derivation details, so that the above equation can be rewritten as:

$$m(x_p) = m_B + x_p \frac{J}{D_p} \left(\frac{\partial H}{\partial q}\right)\bigg|_B + \frac{x_p^2}{2!} \frac{J}{D_p d} \left(\frac{\partial H}{\partial q}\right)\bigg|_B + \ldots \tag{3}$$

where the current density, J, is defined as the discharge current divided by the plate surface area. The terms $\partial H/\partial q$ is a constant and relates the change in hydrogen ion concentration with the change in charge, q. The distance, d, used in the second coefficient is the distance from the center of the cell to the plate's surface.

The concentration where the reaction is occurring, $m(x_R)$, determines the cell potential. The measured cell voltage, V, will be less than this potential due to the voltage drop, V_{drop}, associated with the cell resistance. The cell voltage is calculated using the Nernst equation, and is given as:

$$V = V_0 + \frac{RT}{nF} \ln([H^+]^3[HSO_4^-]) - V_{drop} \qquad (4)$$

where V_0 is the standard electrochemical potential relative to a hydrogen electrode, R the universal gas constant, T the temperature, n the number of electron participating in the reaction, and F the Faraday constant.

The voltage drop of the cell is a function of the resistance, Ω, and the voltage correction, ΔV_i, which is given in Table 1. The voltage correction, ΔV_i, was estimated from the zero current voltage of the cell and used to account for any variation in the initial acid concentration from that used by the model. Both of these terms are used in the voltage drop calculation given below:

$$V_{drop} = \Delta V_i + \Omega I \qquad (5)$$

where I is the discharge current.

The computer model uses the MacLaurin series to estimate the concentration where the reaction occurs. The finite difference equation determines the concentration at the plate's surface, m_B, for use in the series. The distance into the plate where the reaction occurs is calculated from the discharged Ah, the paste density, and the critical volume fraction as discussed in the companion paper [5]. Once this distance is known, the concentration at the reaction site can be calculated and the cell voltage determined from eqn. (4). The model also adds a time correction to the voltage versus time curve to account for the electrolyte stored in the plate, see ref. 5.

The computer model gives the cell voltage as a function of time. From this output, the time to the end of discharge can be determined. The end of discharge usually occurs when a predefined voltage, 1.75 V for this paper, is reached. When the discharge time and current are known, the discharge capacity and hence the utilization of the positive active material can be calculated. In the next section, the voltage versus time and utilization curves generated from the computer model are compared with experimental data.

Comparison with experimental results

Figures 1 and 2 show voltage versus time plots for cells having plates made with positive paste containing 2.2% by weight of glass microspheres. Figure 1 gives the cell voltage as a function of time for discharge rates of 0.034 and 0.087 A/g. Both the experimental and computer-generated curves for these rates are plotted. The experimental voltage curves are from tests previously conducted [1].

A combined plot of the voltage curves at different discharge rates is shown in Fig. 2. One representative experimental curve for each discharge rate is provided with the computer-generated curve. In these Figs., the computer-generated voltage curves provide a reasonable representation to the experimental curves.

Figure 3 shows computer-generated curves of electrolyte concentration as a function of distance. The curves were generated to simulate the discharge of the cell whose voltage versus time curves are plotted in Fig. 1 for the discharge rate of 0.034 A/g. We will use Fig. 3 to explain how the computer model develops the concentration curves as well as the voltage versus time curves. The top curve in Fig. 3 is the concentration at the beginning of the discharge while the bottom curve is the concentration at the end of discharge. In Fig. 3, the negative plate is located at the origin while the dashed line locates the positive plate.
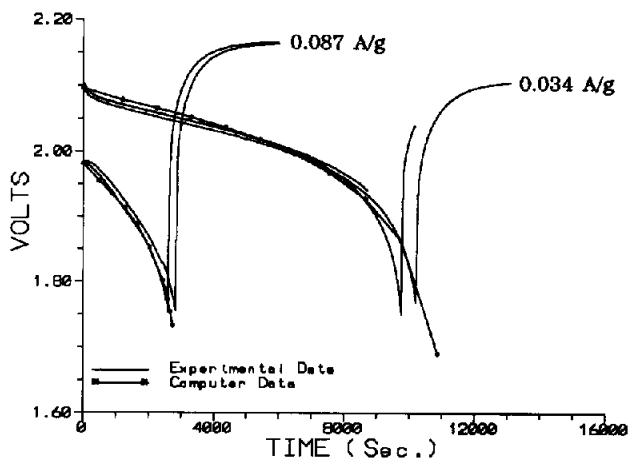
Fig. 1. Cell voltage vs. time for two discharge rates (2.2% by weight of glass microspheres).
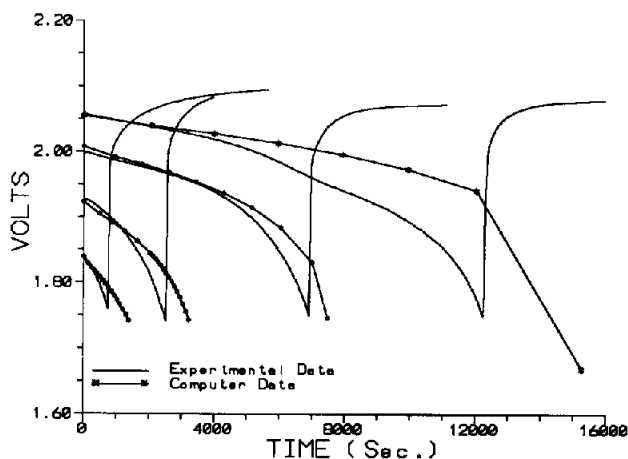

Fig. 2. Combined plot of cell voltage vs. time for different discharge rates (2.2% by weight of glass microspheres).

The finite difference equation provides the concentration for the electrolyte between the plates. The MacLaurin series, eqn. (3), estimate the concentration within the positive plate. The two equations are linked by the concentration at the positive plate's surface, m_B. The form of the MacLaurin series equation does not change with time for a constant-current discharge but does shift downward as the reaction proceeds, see Fig. 3.

The cell voltage depends on the concentration in the plate where the reaction occurs. This distance into the plate changes as the discharge proceeds and is shown in Fig. 3 as the position where the concentration curve ends. At the beginning of the discharge, the reaction occurs at the plate's surface so that the reaction and plate's surface concentrations are the same. At the end of discharge, however, the distance into the plate has grown and the difference in concentration between the surface and where the reaction occurs can be large, see Fig. 3. Once the concentration has been
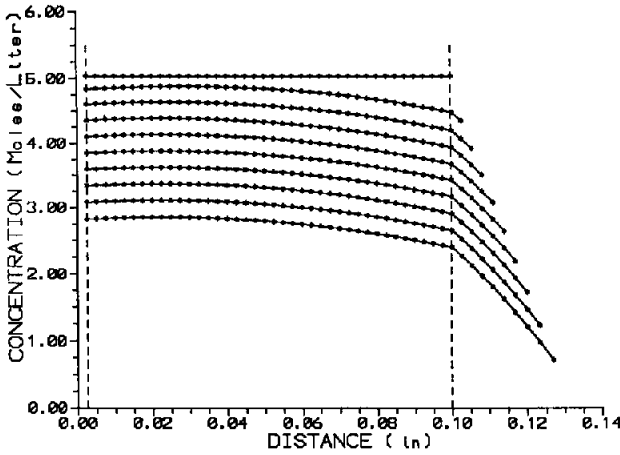
Fig. 3. Concentration vs. distance for 0.034 A/g discharge at different times (2.2% by weight of glass microspheres).
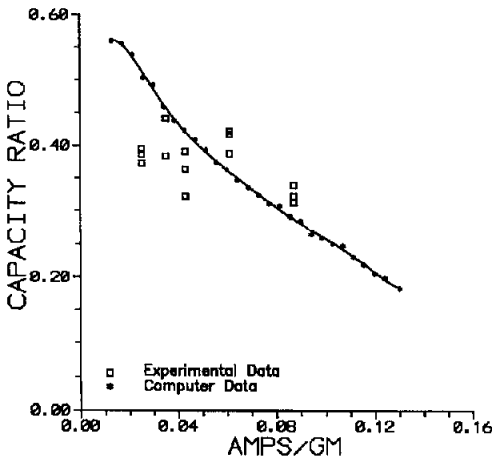

Fig. 4. Capacity vs. specific rate (2.2% by weight of glass microspheres).

established, eqn. (4) can be used to find the cell voltage. After the time correction for the stored electrolyte is made, see ref. 5, the voltage versus time curve can be calculated.

The computer uses concentration curves similar to those of Fig. 3 to generate all the voltage versus time curves shown in this paper. After the discharge time has been found from a particular voltage versus time curve, the plate's capacity at that discharge rate can be calculated. The capacity of a plate can then be found as a function of discharge rate.

Figure 4 shows a plot of capacity versus specific rate for plates having a paste containing a 2.2% loading of glass microspheres. The solid line in Fig. 4 represents the computer-generated data while the experimental data, ref. 1, are shown as boxes in the plot. As can be seen from Fig. 4, the computer curve shows reasonable agreement with the experimental data. Some of the low experimental data points can be attributed

to incomplete formation of the cell so that as the cell was cycled, its capacity increased. The experimental data were taken prior to the model development and not for the purpose of developing the model.

Figure 5 shows voltage versus time curves for cells having positive paste with a 4.4% loading of glass microspheres. Figure 5 is similar to Fig. 2 and shows a combined plot of the voltage curves at different discharge rates. A representative experimental curve is shown in Fig. 5 with each computer-generated curve. These Figs. again show that the computer-generated curves are similar to the experimental curves.

Figure 6 shows capacity as a function of specific rate for plates having paste containing a 4.4% loading of glass microspheres. The boxes shown in the Fig. represent experimental data from ref. 2 and the solid line represents the computer-generated
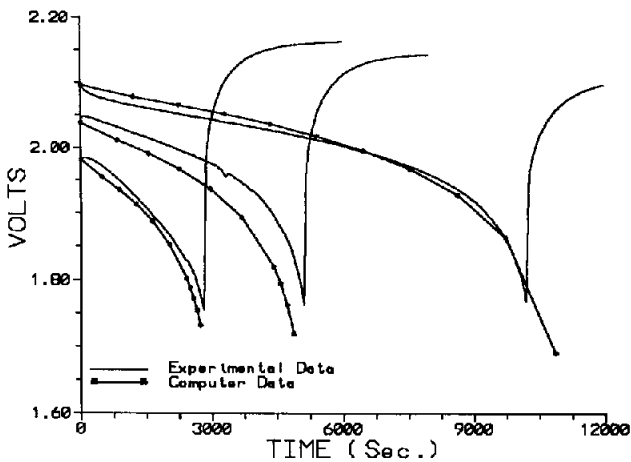

Fig. 5. Combined plot of cell voltage vs. time for different discharge rates (4.4% by weight of glass microspheres).
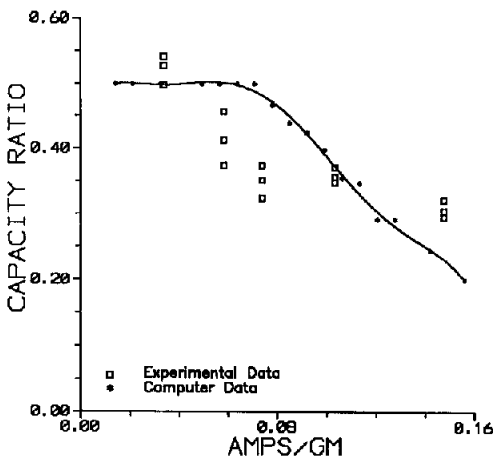

Fig. 6. Capacity vs. specific rate (4.4% by weight of glass microspheres).

data. The computer curve shows reasonable agreement with the experimental data. Again, some of the low experimental data points can be attributed to incomplete formation.

Figures 7 and 8 show curves for plates having a paste containing a 6.6% loading of glass microspheres. Figure 7 shows the voltage versus time curves and Fig. 8 shows the capacity versus specific rate curve for these plates. The computer-generated voltage versus time curves show reasonable agreement with the experimental data. The model, however, does not provide as accurate an initial voltage prediction for the 6.6% plates as it had for the previous plates. The model's capacity curve does show good agreement with the experimental data for these plates except for one high experimental data point around 0.07 A/g.

The parameters characterizing the plates modeled in this paper had a wide range of values. Yet the model provided a reasonable estimate for the performance of all these plates when discharged at constant currents. Although the specific discharge
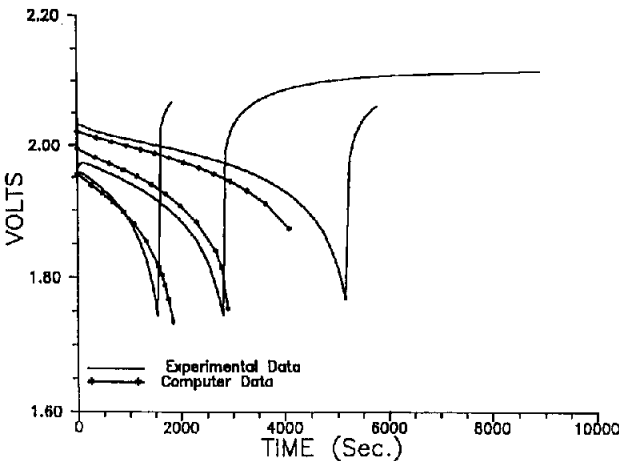
Fig. 7. Combined plot of cell voltage vs. time for different discharge rates (6.6% by weight of glass microspheres).
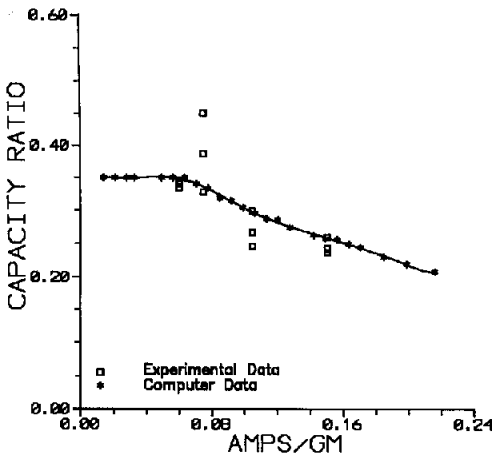
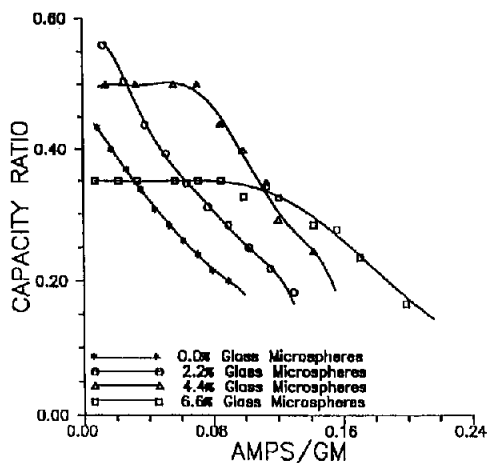Fig. 8. Capacity vs. specific rate (6.6% by weight of glass microspheres).

Fig. 9. Combined plot of capacity vs. specific rate.

rate of the experimental data had a limited range, the different components of the model were well tested. The plates heavily loaded with glass microspheres, 6.6%, were largely limited by paste conductivity while the lightly loaded plates, 2.2%, were diffusion limited. The model also provided a reasonable estimate for the high rate performance of all the plates. The high-rate performance depends upon the amount of electrolyte stored in the plate and the cell's resistance.

Figure 9 summarizes the performance for all the plates modeled in this paper. The Fig. shows the computer-generated curves for capacity as a function of specific rate. In ref. 1, plates with the 4.4% loading of glass microspheres appeared to be close to an optimal loading. At lower, 2.2%, and higher, 6.6%, loadings of glass microspheres, the capacity versus specific rate curves for these plates were lower for all the discharge rates tested. This behavior was believed to result from two competing limiting mechanisms.

The addition of glass microspheres improved plate performance because a higher percentage of active material would react with the electrolyte stored within the plate. This improvement results from a higher ratio of electrolyte stored within the plate to the amount of positive active material. However, the addition of glass microspheres also reduces the paste conductivity. As the amount of glass microspheres in the paste is increased, the conductivity is decreased and will eventually limit a cell's capacity.

Since, the plates were not tested at very low and very high discharge rates, it appears that the 2.2% loading of glass microspheres was optimal. From the model generated curves, we can see that at very low rates (i.e. < 0.02 A/g), the plates with the 2.2% loading would actually provide a higher capacity than the plates with the 4.4% loading. At high discharge rates (i.e. > 0.12 A/g), the 6.6% loaded plates show higher capacities than the 4.4% loaded plates.

Summary and conclusions

This paper used a model presented in a companion paper [5] to predict the performance of plates having different loadings of glass microspheres. The parameters needed by the model to characterize these plates were discussed and provided in Table 1. Voltage versus time curves and capacity versus specific rate curves were

generated by the computer model and compared with experimental data [1]. The experimental and computer-generated curves showed reasonable agreement for all the plates. Since the parameters that characterized the plates had a wide range of values, the agreement between the model and data helps to confirm the model.

In addition, the view incorporated into the model that conductivity limits the low-rate capacity while diffusion limits the capacity at higher rates appears to be validated. The model therefore provides insight into the performance of positive plates having glass microspheres. At medium to high specific rates, glass microspheres can improve a plate's performance because a higher percentage of the plate's active material can react with the electrolyte stored within the plate. The glass microspheres increase the specific volume of the paste so that a better balance occurs between the positive active material and the electrolyte stored within the plate. However, the paste volume must increase if the same amount of active material is used. The glass microspheres take up volume so that the volume performance of the plates may be reduced. The trade-off between specific energy (i.e. energy/weight) and energy density (i.e. energy/volume) will depend on the discharge rates of the application.

At low specific rates, the performance of plates having glass microspheres is reduced because their critical volume fraction is lower. For plates having high loadings of glass microspheres, such as the 6.6% plates, the conductivity of the plates as characterized by the critical volume fraction is so reduced that the only benefits observed occurs at very high discharge rates.

An extension of this work would be to add conductive particles to the positive paste. The conductive particles should eliminate the degradation in plate performance resulting from the loss of active material conductivity. This could result in higher utilizations of positive active material at all discharge rates.

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