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Effect of gelling on the impedance parameters of $Pb/PbSO_4$ electrode in maintenance-free lead-acid batteries

M.P. Vinod *, K. Vijayamohanan

Physical Chemistry Division, National Chemical Laboratory, Pune 411 008, India

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Abstract

The impedance parameters of $Pb/PbSO_4$ electrode in 4.8 M sulfuric acid have been measured potentiostatically under open-circuit conditions over a wide range of frequencies (10^{-2} to 10^4 Hz) under both deep-discharged (state-of-charge, SoC = 0) and fully charged (SoC = 1) conditions. Immobilization of the electrolyte by adding sodium silicate (5 g/l) on the impedance of $Pb/PbSO_4$ electrode shows significant difference in comparison with the flooded system. Four equivalent circuits have been formulated for overcharged and deep-discharged electrodes in gelled and flooded electrolytes, respectively. Impedance parameters are calculated using a phenomenological model, which indicates that in the case of gelled electrolytes, the electrochemical reactions are mass-transfer controlled, in contrast to the flooded electrolyte cells, where the process is known to be charge-transfer controlled. The study provides a non-destructive investigation of the effect of gelling on the electrical performance of sealed maintenance-free lead-acid batteries. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Battery; Gel; Lead-acid; Impedance

1. Introduction

Maintenance-free (MF) lead-acid batteries [1–4] are of present interest for electric vehicle, especially as there is a growing public awareness of the environmental benefit of replacing the gasoline-powered vehicles with low-emission electric vehicles due to environmental benefits. In general, MF lead-acid batteries can be classified into three types: (i) flooded electrolyte type, using low antimony spines in the positive plates and a large volume of reserve electrolyte to compensate for electrolyte loss; (ii) the electrolyte is completely absorbed in a glass-fiber separator and MF operation is achieved by using an internal oxygen cycle; (iii) the electrolyte is rendered immobilized using organic or inorganic thixotropic agents [5], such as polymethyl methacrylate and colloidal silica. Although the original driving force for immobilizing the electrolyte was purely safety reasons, later gelling was observed to favorably affect the performance and life of these batteries [6]. For example, in gelled electrolyte batteries, loss of water during overcharge either as hydrogen or oxygen is negligible and no topping-up is necessary. In addition, gelled electrolyte cells are virtually unaffected by acid stratification. More significantly, the immobilization of electrolyte by gelling permits the production of sealed batteries with highly improved cycle-life and high-charge acceptance. Finally, these types of batteries are useful in specific applications such as rural area power supplies and solar energy storage, unlike their flooded counterparts.

After the wide introduction of gelled batteries, the question of how gelling affects the electrochemistry of lead-acid batteries has become significant. Several attempts to design spill-proof lead-acid batteries with the aid of gelled electrolytes has been carried out for last few decades inspired from the efficient application of all solid primary batteries. Initially, the method to immobilize the electrolyte was improved to achieve simple spill-proof lead-acid batteries with certain cycle-life stability. Subsequently, a combination with valve regulated (VRLA) characteristics, yielded all the essential features of MF lead-acid batteries. An immediate consequence of gelling was the decrease in the freely available H_2SO_4 concentration and

* Corresponding author. Tel.: +91-020-5893044.
E-mail address: viji@ems.ncl.res.in (M.P. Vinod).

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an increase in the overall viscosity of the solution. These results were further supported by the recent studies, which show that gelling affects even the electrode kinetics of both hydrogen evolution reaction [7] and the oxygen reduction reaction [8]. More significant are the changes in the double-layer capacitance and uncompensated resistance of the $Pb/PbSO_4$ electrode reaction as a result of gelling. Although not a practical technique for field applications, impedance methods are very useful for the study of the mechanism and failure modes of electrode processes of lead-acid batteries in a carefully controlled laboratory environment. The impedance methods are accurate, fast, and are non-destructive in nature. As a result, impedance measurements are widely used for analyzing an interfacial process in lead-acid batteries [9–16]. Most of these studies are for state-of-charge (SoC) determination and failure mode analysis from the measurement of the impedance parameters of electrodes during various SoCs with the help of appropriate equivalent circuits [9,10,12,14].

This paper deals with the effect of a thixotropic agent, namely, sodium silicate, on the impedance parameters of the $Pb/PbSO_4$ negative electrode. More specifically, the impedance is investigated in flooded and gelled electrolyte cells in fully charged (SoC = 1) and deep discharged (SoC = 0) states using four appropriate Randle types of equivalent circuits. Among the various impedance parameters, those which have direct relevance to design, life and performance characteristics of an electrode, namely R_{ct}, C_{dl} and $R_{\Omega,}$ are specially studied in order to understand the influence of gelling. Thus, impedance analysis is a non-destructive method for investigating the effect of gelling on these parameters and such a study will be helpful in improving the performance of VRLA batteries.

2. Experimental details

Positive and negative lead-acid plates were obtained in a factory cured and formed condition. The experimental details of formation of the cell are described elsewhere [7,17]. All the electrode materials were made using the same grid materials namely, Pb–Ca (0.08 wt.%)–Sn (0.5 wt.%), to exclude possible effects of interaction by corrosion products. A typical cell was assembled in 4.8 M sulfuric acid with a positive counter electrode (PbO_2) on either side of the working electrode along with a pre-calibrated Hg/Hg_2SO_4, 4.8 M H_2SO_4 reference electrode. All the potentials in this study are reported versus this reference electrode. The reference electrode was connected to the test cell with a Luggin capillary tip aligned close to the working electrode to minimize the uncompensated resistance due to the solution. The cell was subjected to galvanostatic charging and discharging for five cycles to stabilize the capacity. The discharge and charge cut-off points for these cycles were −0.85 and −1.2 V. A small piece (1 cm^2 geometric area) of lead electrode from a fully charged and from a deeply discharged cell was used for the impedance analysis.

The impedance measurements were carried out potentiostatically using a lead electrode as the working electrode in 4.8 M sulfuric acid. A platinum foil was used as the counter electrode rather than a PbO_2 electrode, in order to exclude the contribution of the resistance of the counter electrode to the total impedance of the system. All the experiments were conducted by means of a PAR 283 potentiostat coupled to a PAR 5210 Lock-in amplifier with computer controlled data acquisition systems. The experiments were repeated with immobilized electrolyte having the same sulfuric acid concentration. Immobilization of the electrolyte was achieved by using sodium silicate as a thixotropic agent (5 g dm^{-3}) [18]. Low viscosity is maintained with occasional stirring prior to the measurements. The impedance spectrum was recorded in the frequency range 10^{-2} to 10^4 Hz. Once the desired potential was achieved, the current was switched off and after a period of rest, measurements were carried out under open-circuit conditions. All experiments were performed at a temperature of 25 ± 1°C, which was controlled by a thermostat.

3. Results and discussion

The impedance response of a corroding lead electrode in sulfuric acid has been reported to be under charge-transfer control [11]. It is known that for different SoCs of the active material of the $Pb/PbSO_4$ electrode, the impedance plot over a wide range of frequencies is a semi-circle with its radius continuously diminishing with decrease in SoC [11].

The corroding surface can be represented fairly well by the equivalent circuit shown in Fig. 1, where R_Ω is the ohmic resistance of the corrosion products deposited on the electrode surface, and also has contributions from the resistance of the electrical leads and the electrical connections to the electrode, C_{dl} is the capacitance of the electrical double-layer at the metal–solution interface formed by absorbed molecules and ions, and R_{ct} is the charge-transfer resistance of the rate-controlling electrochemical reaction of the corrosion process .The impedance spectrum has also a very strong dependence on the viscosity and the density of the sulfuric acid, which can be understood in terms of the variation of specific resistivity of sulfuric acid with density [19].

The pasted negative plate used is a typical example for a porous battery electrode. The porosity is a strong function of the SoC of the electrode. The composition of the active material, as well as associated the impedance parameters, changes continuously with the duration of charge–discharge. The porous nature of the active material is helpful in improving the utilization coefficient. The electrochemical performance of the electrodes is deter-

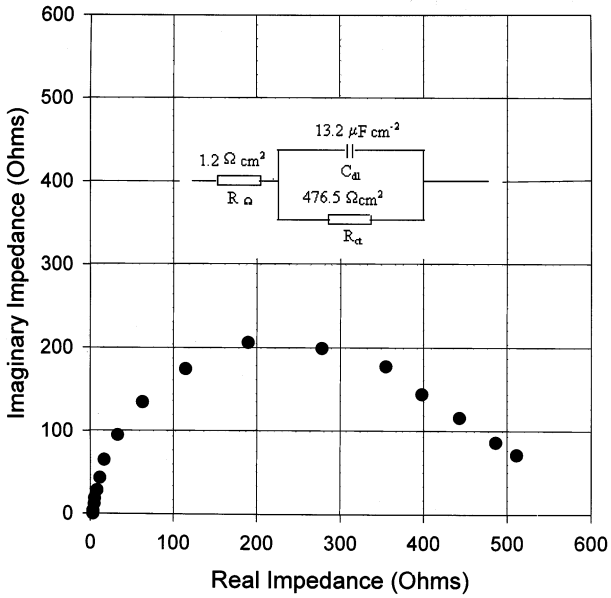

Fig. 1. Impedance plot for the fully charged $Pb/PbSO_4$ electrode (SoC = 1) in 4.8 M sulfuric acid measured at open-circuit voltage using Pt foil counter electrode and Hg/Hg_2SO_4, 4.8 M H_2SO_4 reference electrode, in frequency range 10^{-2} to 10^4 Hz.

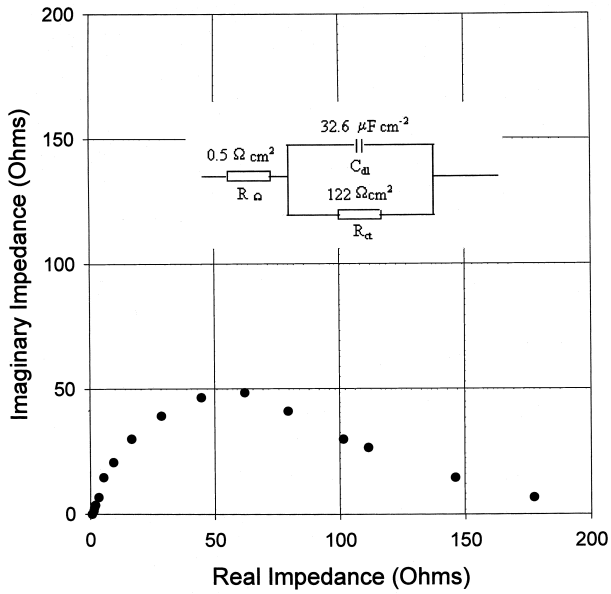

Fig. 2. Impedance plot for deep-discharged $Pb/PbSO_4$ electrode (SoC = 0) in 4.8 M sulfuric acid measured at open-circuit voltage using Pt foil counter electrode and Hg/Hg_2SO_4, 4.8 M H_2SO_4 reference electrode, in frequency range 10^{-2} to 10^4 Hz.

mined by a number of factors, e.g., including the kinetics of the electrochemical reaction, the rate of mass-transfer to the electrode surface, and the current distribution in the electrode. The current distribution is determined to a large extent by the effective conductivity (porous electrode matrix and electrolyte in the pores which in turn depends on the pore-size distribution), and will change depending on the composition changes during the charge–discharge processes.

Impedance spectra of the $Pb/PbSO_4$ electrode in 4.8 M H_2SO_4 obtained from a fully charged electrode and a deep-discharged electrode are shown in Figs. 1 and 2, respectively. A detailed discussion is available in Ref. [16] based on the semi-circle fitting over a wide range of frequencies. The radius of the semi-circle is found to decrease with the SoC. This is probably due to a decrease in R_{ct} as the electro-active material is consumed. The centres of the semi-circles are slightly dispersed from the horizontal axis. This frequency dispersion is typical of a corroding electrode/electrolyte interface and originates from the additional dependence of the impedance on frequency.

The major potential-determining reactions of the $Pb/PbSO_4$ electrode under open-circuit conditions are:

$$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-} \quad E_o = -0.9716 \tag{1}$$

$$2H^+ + 2e^- \rightarrow H_2 \quad E_o = -0.6186 \tag{2}$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad E_o = 0.6116 \tag{3}$$

At higher SoC values, the observed potential is a corrosion potential and has contributions from anodic lead dissolution and cathodic hydrogen evolution. At low SoC values, the hydrogen evolution reaction is thermodynamically feasible, and the presence of large amounts of $PbSO_4$ demands Pb^{2+} reduction as the major potential-determining reaction. This reaction is charge-transfer controlled and an equivalent circuit of Randle type will approximately represent the electrochemical properties of the $Pb/PbSO_4$electrode.

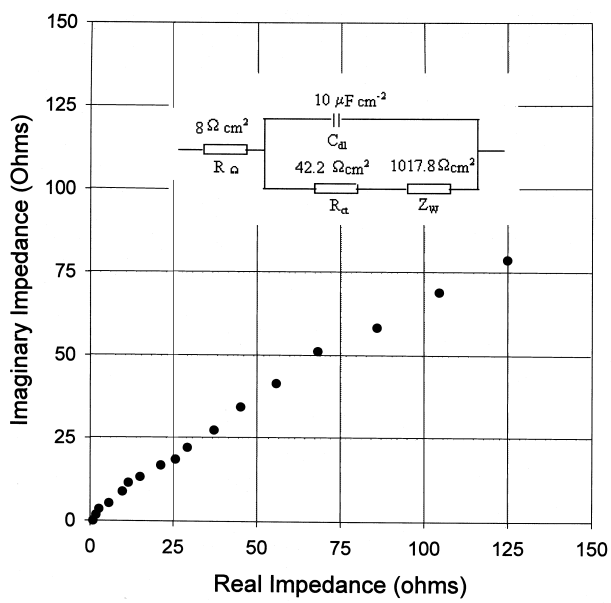

Fig. 3. Impedance plot for fully charged $Pb/PbSO_4$ electrode (SoC = 1) in 4.8 M sulfuric acid immobilized using 5 g dm^{-3} sodium silicate, measured at open-circuit voltage using Pt foil counter electrode and Hg/Hg_2SO_4, 4.8 M H_2SO_4 reference electrode, in frequency range 10^{-2} to 10^4 Hz.

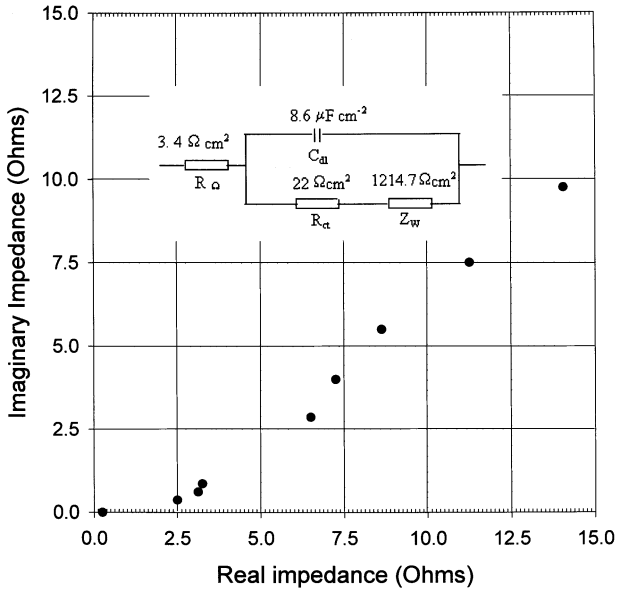

Fig. 4. Impedance plot for deep-discharged $Pb/PbSO_4$ electrode (SoC = 0) in 4.8 M sulfuric acid immobilized using 5 g dm^{-3} sodium silicate, measured at open-circuit voltage using Pt foil counter electrode and Hg/Hg_2SO_4, 4.8 M H_2SO_4 reference electrode, in frequency range 10^{-2} to 10^4 Hz.

In contrast to the impedance spectrum in flooded electrolytes, the spectrum for $Pb/PbSO_4$ electrodes in gelled electrolytes shows no semi-circle, both at high and as low SoC values as shown in Figs. 3 and 4. The impedance spectrum is linear and is observed only in the high frequency region. This shows that the electrochemical processes in the gelled electrolyte are limited by the mass-transfer process on the $Pb/PbSO_4$ electrode surface, rather than by the charge-transfer process, as observed in the flooded electrolyte. The increase in hindrance of mass-transfer, is possibly caused by the presence of an interpenetrating network of polysilicic acid gel that limits the electrochemical response. Thus, the equivalent circuit in this case can be formulated by adding a Warburg component to the normal Randle equivalent circuit, as shown in Figs. 3 and 4.

The analysis of the impedance data presented in Figs. 1–4 allows the formulation of four equivalent circuits for overcharged and deep-discharged $Pb/PbSO_4$ electrodes in flooded and gelled electrolytes. These equivalent circuits, along with the magnitudes of impedance parameters, are also presented in the respective figures. The resistance and capacitance values are calculated using a semi-circle fit in the case of flooded electrolyte and a linear fit in the case of a gelled electrolyte. A summary of the important electrochemical parameters of the $Pb/PbSO_4$ electrode in flooded and gelled electrolytes evaluated by this method is given in Table 1, which clearly shows the drastic effects of gelling. For example, the ohmic resistance values for fully charged electrodes are increased from 1.19 Ω in a flooded system to 7.97 Ω cm^2 in gelled electrolytes. Perhaps, one major contribution to the increased ohmic resistance at high SoC values arises from the adsorbed hydrogen. The silicate network can act as a surface layer and as a result, the rate of evolution of hydrogen will be retarded in the gelled electrolytes. In contrast to the ohmic resistance contribution, the charge-transfer resistance values are decreased as a result of gelling for both overcharged and deep-discharged electrodes. This is probably due to the fact that as result of increased hindrance to mass-transfer, the charge-transfer becomes less important in gelled electrolytes. In comparison, the double-layer capacitance values are slightly decreased as a result of gelling. This effect is more pronounced for an overcharged electrode. This is because of the contribution from adsorbed hydrogen, which is enhanced by the presence of silicate ions. Earlier ESCA studies [20] show no evidence of chemisorbtion of Si on Pb. This may be due to the very high rate of hydrolysis of Pb–O–Si in highly acidic conditions. Under those experimental conditions, the electrode in a flooded electrolyte has no contribution from Warburg impedance, while in a gelled electrolyte, the Warburg impedance is significantly high. From the Warburg impedance, the diffusion coefficient of Pb^{2+} ions in sulfuric acid can be calculated. At high frequencies, the Warburg impedance for Pb^{2+} ions in sulfuric acid is given by [16]:

$$Z_w = \frac{RT}{n^2F^2C_{Pb}^{2+}\sqrt{D_{Pb}^{2+}}} \tag{4}$$

Literature data gives the solubility of Pb^{2+} in 5 M H_2SO_4 at 20°C as 4.4×10^{-6} M [21]. Assuming that gelling has no effect on the solubility of Pb^{2+} ions in sulfuric acid, the diffusion coefficient, $D_{Pb^{2+}}$, in gelled electrolyte can be calculated using the Warburg impedance values obtained

Table 1
Effect of gelling on impedance properties of $Pb/PbSO_4$ electrode

Cell type	R_Ω (Ω cm^2)	R_{ct} (Ω cm^2)	C_{dl} (μF cm^{-2})	$I_{o,Pb}$ (A $cm^{-2} \times 10^{-6}$)	σ (Ω cm^2 $s^{-1/2}$)	D_o^a (cm^2 $s^{-1} \times 10^{-6}$)
Flooded, fully charged	1.2	476.5	13.2	26.9	–	–
Flooded, deeply discharged	0.5	122	32.6	105.2	–	–
Gelled, fully charged	8.0	42.2	10.0	304.3	1017.8	0.22
Gelled, deeply discharged	3.4	22	8.6	583.8	1214.7	0.14

[a]Based on the specific surface area of lead in sulfuric acid (10^3 cm^{-2}).

from the equivalent circuit. The specific surface area of lead in sulfuric acid at various SoC is of the order of 10^3 cm^{-1} [16]. Thus, it is found that the diffusion coefficient is 2.2×10^{-7} and 1.5×10^{-7} cm^2/s in fully discharged and deep-discharged electrolytes, respectively. These values can be compared with the diffusion coefficient of Pb^{2+} ions in 5 M sulfuric acid reported as 2.3×10^{-6} cm^2/s [21]. Thus, an order of magnitude decrease is observed for the diffusion coefficient in gelled electrolyte. This is presumed to arise from an increased hindrance to mass-transfer by the presence of the three-dimensional network of silica gel. There is also a possible contribution from the more compact diffusion layer in gelled electrolyte than in flooded electrolyte. The assumption that solubility is not affected by gelling is not valid in general and low solubility may also partly account for the low values of diffusion coefficient. The variation of diffusion coefficient with state of charge is not too large and all the data fall within the same order of magnitude.

4. Conclusions

A systematic impedance analysis of the effect of gelling on the $Pb/PbSO_4$ electrodes shows drastic change in the electrochemistry of these electrodes. Although charge-transfer resistance (R_{ct}) values decrease in gelled electrolyte, the ohmic resistance (R_Ω) of the $Pb/PbSO_4$ is increased. There is a drastic increase in Warburg impedance in gelled electrolyte, which is almost negligible in flooded, electrolyte. Thus, gelling of the electrolyte causes the electrochemical processes to be limited by mass-transfer.

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