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Short communication

# Extracting equivalent circuit parameters of lead–acid cells from sparse impedance measurements

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**Abstract**

A method for extracting the equivalent circuit parameters of a lead–acid battery from sparse (only three) impedance spectroscopy observations at three different frequencies is outlined. The method is ideal for finding the parameters in an equivalent circuit consisting of bulk resistance, a reaction resistance and a constant phase element (CPE). Electrochemical impedance spectroscopy (EIS) measurements were made on spirally wound 2.5 Ah lead–acid cells. The equivalent circuit parameters found using our method closely compare with those extracted from the EIS measurements. The complete EIS spectrum calculated using the estimated circuit parameters at all other frequencies also closely matched the actual measurements.


*Keywords:* Lead–acid batteries; Electrochemical impedance spectroscopy; Equivalent circuits; Constant phase element

## 1. Introduction

The value and importance of electrochemical impedance spectroscopy (EIS) in the study of electrochemical power sources, such as batteries and fuel cells, is well documented [1–7]. It is known that EIS serves as a powerful tool to characterize electrochemical processes occurring in a cell and to thereby estimate useful cell/battery parameters such as state of charge (SOC), cranking power, remaining service life, etc. [8]. The mathematical theory describing the exact electrochemical processes (such as mass transport, electrode reaction kinetics, charge transfer, etc.) is complex. Therefore, equivalent circuit models of electrochemical power sources are widely used to describe the macroscopic behavior of the electrodes, separator, and electrolyte in an electrochemical cell. The small-signal behavior of an equivalent circuit model bears a correspondence with the terminal properties of the battery over a band of frequencies. The general approach to extracting equivalent circuit parameters of an electrochemical cell is to measure the EIS spectrum of the cell over a wide frequency range and then use a complex least squares analysis approach to curve fit the EIS spectrum [4].

In a recent disclosure, Champlin has proposed a new technique involving measurement of real and imaginary parts of the complex immitance of a cell at $n$ ($\geq$2) discrete frequencies to extract the component values of an equivalent circuit consisting of $2n$ circuit elements [8]. The configuration chosen is a series RL circuit and a few parallel RC sections all connected in series. The advantages of this approach over the conventional method are: (1) the equivalent circuit parameters are extracted *exactly* using a closed form solution of the equivalent circuit equations (rather than being *estimated* through a curve fitting technique), and (2) the complex immitance measurements need only be made at a few discrete frequencies rather than being made over a wide range of frequencies. The limitation of the approach, however, is that the single RC networks only provide single time constants for the electrochemical processes at an electrode and it is widely recognized that the electrochemical processes at electrodes usually comprise multiple time constants, which are often treated in a distributed manner (rather than using lumped element parameters) [9].

To make the circuit model more consistent with the actual processes taking place across the electrochemical interface, Cole and Cole [9] found it expedient to introduce a hypothetical element called a constant phase element (CPE). The combination of several RC sections can be used to approximate a CPE element. In this paper, we present closed form expressions for the model parameters for an equivalent circuit comprising a parallel CPE-R ($R_R$) network in series with a resistor, $R_\infty$, representing the bulk series resistance of

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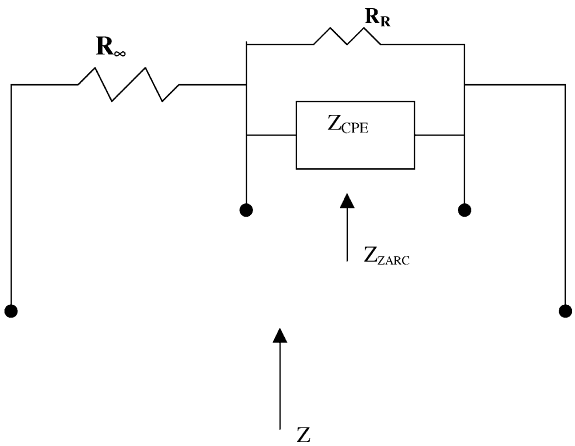


Fig. 1. Equivalent circuit model of lead–acid cell at high SOC.

the electrochemical cell (see Fig. 1). The impedance of the parallel CPE-$R_R$ combination is also called the ZARC impedance denoted by $Z_{ZARC}$ because the Nyquist plot for a cell modeled by this equivalent circuit exhibits a depressed arc. The $Z_{ZARC}$ impedance results from having to represent a distributed time constant in the description of electrochemical processes [4].

We first present the mathematical derivation of the equivalent circuit model parameters from the real and imaginary parts of the complex impedance. This is followed by a description of experimental measurements made on 2.5 Ah spirally wound lead–acid cells. Finally, the application of the method to extraction of the equivalent circuit parameters for a single set of lead–acid cell impedance data (from only three data points) and the reproduction of the entire measurement spectrum using the extracted equivalent circuit model will be described.

## 2. The mathematical derivation

Consider the circuit shown in Fig. 1.

$Z_{CPE}$ represents the constant phase element whose impedance is given by

$$Z_{CPE}\frac{1}{A_o(j\omega)^{\psi_{ZC}}} \tag{1}$$

where $A_o$ and $\psi_{ZC}$ are two parameters to be found. $R_R$ is called the reaction resistance and comes in shunt with the CPE.

Then $Z_{ZARC}$ becomes

$$\frac{R_R}{1+R_RA_o(j\omega)^{\psi_{ZC}}} \tag{2}$$

The combined impedance $Z$ of the entire circuit in Fig. 1 becomes

$$Z = R_\infty + Z_{ZARC} \tag{3}$$

Now let us denote the real part, imaginary part and square of the absolute value of $Z$ as

$$Z' = \mathrm{Re}\{Z\} \tag{4}$$

$$Z'' = \mathrm{Im}\{Z\} \tag{5}$$

$$|Z|^2 = \{Z^{2\prime} + Z^{2\prime\prime}\} \tag{6}$$

We can explicitly obtain expressions for $Z'$ and $Z''$. For convenience let us introduce,

$$\chi = \frac{\psi_{ZC}\pi}{2} \tag{7}$$

$$\Lambda_1 = R_RA_o\omega^{\psi_{ZC}} \tag{8}$$

$$\Lambda_2 = 1 + \Lambda_1^2 + 2\Lambda_1\cos\chi \tag{9}$$

$$Z' = R_\infty + \frac{R_R}{\Lambda_2}(1+\Lambda_1\cos\chi) \tag{10}$$

$$Z'' = \frac{-R_R\Lambda_1\sin\chi}{\Lambda_2} \tag{11}$$

Eliminating $\Lambda_2$ from Eqs. (10) and (11), we can derive for $\Lambda_1$ as

$$\Lambda_1 = \frac{-Z''}{((Z'-R_\infty)\sin\chi + Z''\cos\chi)} \tag{12}$$

It is possible to interrelate the quantities in Eqs. (4)–(6). Towards this end, we introduce

$$\zeta_1 = 2R_\infty + R_R \tag{13}$$

$$\zeta_2 = R_\infty\cot\chi \tag{14}$$

$$\zeta_3 = -R_\infty^2 - R_RR_\infty \tag{15}$$

With some algebraic work we get,

$$\zeta_1Z' + \zeta_2Z'' + \zeta_3 = |Z|^2 \tag{16}$$

By solving for $\zeta$'s we can get the component values of the circuit of Fig. 1. Suppose Eq. (16) is enforced at three frequencies, say, $\omega_i$, $i = 1$, 2, and 3, where $Z'$, $Z''$ and $|Z|^2$ are denoted with corresponding subscripts we arrive at

$$\begin{bmatrix} Z_1' & Z_1'' & 1 \\ Z_2' & Z_2'' & 1 \\ Z_3' & Z_3'' & 1 \end{bmatrix}\begin{bmatrix}\zeta_1\\ \zeta_2\\ \zeta_3\end{bmatrix} = \begin{bmatrix}|Z|_1^2\\ |Z|_2^2\\ |Z|_3^2\end{bmatrix} \tag{17}$$

Solving Eq. (17) we get $\zeta$'s. Also note that from Eqs. (13) and (15),

$$R_R^2 = \zeta_1^2 + 4\zeta_3 \tag{18}$$

$$\sin^2\chi = \frac{R_R^2}{\zeta_1^2+\zeta_2^2+4\zeta_3} \tag{19}$$

$$\chi = \sin^{-1}\left(\frac{R_R}{\sqrt{\zeta_1^2+\zeta_2^2+4\zeta_3}}\right) \tag{20}$$

Hence,

$$R_R = \sqrt{\zeta_1^2 + 4\zeta_3} \quad (21)$$

$$R_\infty = \frac{(\zeta_1 - R_R)}{2} \quad (22)$$

$$\psi_{ZC} = \frac{2}{\pi}\sin^{-1}\left(\frac{R_R}{\sqrt{\zeta_1^2 + \zeta_2^2 + 4\zeta_3}}\right) \quad (23)$$

From Eqs. (8), (12) and (22), we can find $A_o$ as follows. With the aid of the quantities found above and in terms of one of the frequencies $\omega_i$ we can derive,

$$A_o = \frac{-Z_i''}{(R_R\omega_i^{\psi_{ZC}})((Z_i' - R_\infty)\sin\chi + Z_i''\cos\chi)} \quad (24)$$

Eqs. (21)–(24) show how to find the sought-for parameters.

## 3. Extraction of equivalent circuit parameters for lead–acid cells

A Solartron 1280B Electrochemical Measurement Unit (combined potentiostat/galvanostat and frequency response analyzer) was used to measure the Electrochemical Impedance of 2.5 Ah Hawker 'D'-size lead–acid cells at 80% SOC over the frequency range 1–200 Hz. ZPlot and ZView software were used to extract equivalent circuit parameters assuming the model of Fig. 1. This software estimates the equivalent circuit parameters using the complex nonlinear least squares curve fitting technique. The impedance data and the estimated parameters are

Table 1
Electrochemical impedance measurements made by Solartron SI 1280B over the frequency band 1–200 Hz

| Observations (no.) | Frequency (Hz) | Real part of impedance $Z'$ (Ω) | Imaginary part of Impedance $Z''$ (Ω) |
|---|---|---|---|
| 1 | 200.0000 | 0.0129 | −0.0008 |
| **2** | **158.9000** | **0.0130** | **−0.0011** |
| 3 | 126.2000 | 0.0131 | −0.0015 |
| 4 | 100.2000 | 0.0132 | −0.0018 |
| 5 | 79.6000 | 0.0135 | −0.0025 |
| 6 | 63.2000 | 0.0137 | −0.0031 |
| 7 | 50.2000 | 0.0140 | −0.0037 |
| 8 | 39.9100 | 0.0145 | −0.0045 |
| 9 | 31.7000 | 0.0149 | −0.0054 |
| **10** | **25.1800** | **0.0156** | **−0.0064** |
| 11 | 20.0000 | 0.0165 | −0.0075 |
| 12 | 15.8900 | 0.0177 | −0.0088 |
| 13 | 12.6200 | 0.0191 | −0.0101 |
| 14 | 10.0200 | 0.0210 | −0.0113 |
| 15 | 7.9600 | 0.0230 | −0.0125 |
| 16 | 6.3200 | 0.0255 | −0.0133 |
| 17 | 5.0200 | 0.0281 | −0.0137 |
| 18 | 3.9910 | 0.0308 | −0.0139 |
| 19 | 3.1700 | 0.0333 | −0.0136 |
| 20 | 2.5180 | 0.0357 | −0.0131 |
| **21** | **2.0000** | **0.0378** | **−0.0124** |
| 22 | 1.5890 | 0.0396 | −0.0119 |
| 23 | 1.2620 | 0.0412 | −0.0113 |
| 24 | 1.0020 | 0.0426 | −0.0106 |
| 25 | 1.0000 | 0.0427 | −0.0106 |
| Parameters estimated by Zview software: $R_\infty = 0.012647$ Ω, $R_R = 0.035631$ Ω, $A_o = 1.816$, $\psi_{ZC} = 0.85186$ | | Parameters extracted using Eqs. (21)–(24): $R_\infty = 0.01269974960794$ Ω, $R_R = 0.03550897543974$ Ω, $A_o = 1.79656589706058$, $\psi_{ZC} = 0.84999961293183$ | |

The sparse observations used in the algorithm are given in bold.

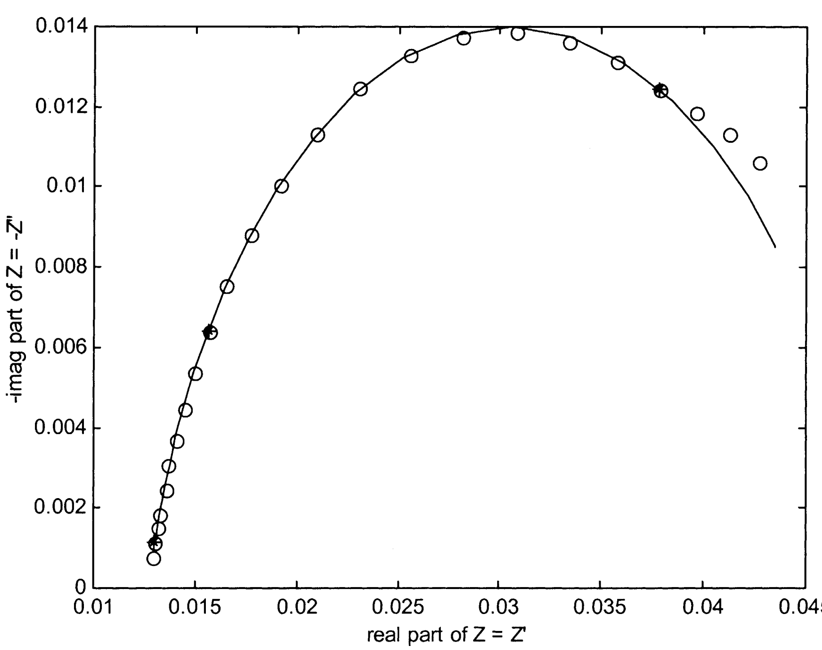


Fig. 2. Impedance values over the frequency band 1–200 Hz. Circles indicate the actual measurements made using Solartron SI 1280B. Among the 25 observations only three marked by asterisks are used to estimate the circuit parameters and impedance calculated using these parameters is shown by dotted line. Note that both the Nyquist plots match almost everywhere except at very low frequencies.

shown in Table 1. Next, we selected three frequencies, 158.9 Hz, 25.18 Hz and 2 Hz corresponding to observations 2, 10 and 21 (indicated in larger bold font in Table 1) and extracted the equivalent circuit parameters using Eqs. (21)–(24). In the Appendix A we provide MATLAB code used to obtain the results. Fig. 2 shows superposition of the Nyquist plot of the measured impedance (circles) and the impedance calculated using the equivalent circuit parameters extracted from the three frequencies (dotted line). Note that the ordinate refers to the negative imaginary part of impedance and the three observations used in the estimation process are shown by asterisks. A close agreement between the measured and calculated response is seen except at very low frequencies. The discrepancy at low frequencies can be explained by the transition in this frequency range to a diffusion-dominated electrochemical process which would not be described by the present equivalent circuit (this part of the EIS spectrum is usually modeled by the Warburg impedance [4]).

## 4. Conclusions

In this paper, we have described a new technique for extracting equivalent circuit parameters for lead–acid cells that may be modeled by a bulk resistance in series with a parallel CPE element/resistor combination using impedance measurements made at only three frequencies. This method provides the *exact* values of the equivalent circuit parameters rather than estimating them from a nonlinear curve fitting technique. The measured impedance spectrum for a spirally wound lead–acid cell was accurately reproduced using EIS measurements at three different frequencies.

## Appendix A

```
%sp3alg.m    %%%% sparse algorithm
%% MATLAB Code to estimate circuit parameters
%%%% using only three (EIS) observations
clear
%Freq(Hz)     Ampl         Bias         Time(Sec)     Z'(a)      Z''(b)       GD        Err Range"
% Measured Data
Data=[
2.000000E+02, 4.0000E-02, 0.0000E+00, 8.568000E+01, 1.2873E-02,-7.6375E-04, 0.0000E+00, 0, 2
1.589000E+02, 4.0000E-02, 0.0000E+00, 8.964000E+01, 1.3015E-02,-1.1471E-03, 0.0000E+00, 0, 2
1.262000E+02, 4.0000E-02, 0.0000E+00, 9.361000E+01, 1.3144E-02,-1.5282E-03, 0.0000E+00, 0, 2
1.002000E+02, 4.0000E-02, 0.0000E+00, 9.780000E+01, 1.3246E-02,-1.8488E-03, 0.0000E+00, 0, 2
7.960000E+01, 4.0000E-02, 0.0000E+00, 1.019900E+02, 1.3536E-02,-2.4589E-03, 0.0000E+00, 0, 2
6.320000E+01, 4.0000E-02, 0.0000E+00, 1.061700E+02, 1.3657E-02,-3.0984E-03, 0.0000E+00, 0, 2
5.020000E+01, 4.0000E-02, 0.0000E+00, 1.103600E+02, 1.4012E-02,-3.6786E-03, 0.0000E+00, 0, 2
3.991000E+01, 4.0000E-02, 0.0000E+00, 1.143200E+02, 1.4461E-02,-4.4634E-03, 0.0000E+00, 0, 2
3.170000E+01, 4.0000E-02, 0.0000E+00, 1.185100E+02, 1.4948E-02,-5.3857E-03, 0.0000E+00, 0, 2
2.518000E+01, 4.0000E-02, 0.0000E+00, 1.225800E+02, 1.5627E-02,-6.3932E-03, 0.0000E+00, 0, 2
2.000000E+01, 4.0000E-02, 0.0000E+00, 1.268800E+02, 1.6451E-02,-7.5452E-03, 0.0000E+00, 0, 2
1.589000E+01, 4.0000E-02, 0.0000E+00, 1.310700E+02, 1.7657E-02,-8.8192E-03, 0.0000E+00, 0, 2
1.262000E+01, 4.0000E-02, 0.0000E+00, 1.362400E+02, 1.9109E-02,-1.0066E-02, 0.0000E+00, 0, 2
1.002000E+01, 4.0000E-02, 0.0000E+00, 1.406500E+02, 2.0950E-02,-1.1335E-02, 0.0000E+00, 0, 2
7.960000E+00, 4.0000E-02, 0.0000E+00, 1.448400E+02, 2.3027E-02,-1.2501E-02, 0.0000E+00, 0, 2
6.320000E+00, 4.0000E-02, 0.0000E+00, 1.492400E+02, 2.5482E-02,-1.3288E-02, 0.0000E+00, 0, 2
5.020000E+00, 4.0000E-02, 0.0000E+00, 1.538800E+02, 2.8112E-02,-1.3743E-02, 0.0000E+00, 0, 2
3.991000E+00, 4.0000E-02, 0.0000E+00, 1.580500E+02, 3.0785E-02,-1.3889E-02, 0.0000E+00, 0, 2
3.170000E+00, 4.0000E-02, 0.0000E+00, 1.625700E+02, 3.3327E-02,-1.3632E-02, 0.0000E+00, 0, 2
2.518000E+00, 4.0000E-02, 0.0000E+00, 1.671000E+02, 3.5678E-02,-1.3141E-02, 0.0000E+00, 0, 2
2.000000E+00, 4.0000E-02, 0.0000E+00, 1.710500E+02, 3.7822E-02,-1.2444E-02, 0.0000E+00, 0, 2
1.589000E+00, 4.0000E-02, 0.0000E+00, 1.755700E+02, 3.9603E-02,-1.1862E-02, 0.0000E+00, 0, 2
1.262000E+00, 4.0000E-02, 0.0000E+00, 1.808700E+02, 4.1168E-02,-1.1316E-02, 0.0000E+00, 0, 2
1.002000E+00, 4.0000E-02, 0.0000E+00, 1.871400E+02, 4.2620E-02,-1.0628E-02, 0.0000E+00, 0, 2
1.000000E+00, 4.0000E-02, 0.0000E+00, 1.911000E+02, 4.2664E-02,-1.0620E-02, 0.0000E+00, 0, 2];
dth=[2 10 21];%%% Feed which three observations are used.
w=2*pi*Data(dth,1); % radian frequency
Zx=Data(dth,5); %% real part of Z denoted by Z' in the text
Zy=Data(dth,6); %% Imag part of Z denoted by Z'' in the text
Zsq=Zx.^2+Zy.^2;  %%% Mag square |Z|^2 of the impedance
u=ones(3,1);
inv([Zx Zy u])*Zsq;   % solving the three simultaneous equations
zeta1=ans(1);
zeta2=ans(2);
zeta3=ans(3);
%%%%%%%%%%%%%%%%%%%%%%%  Estimation follows
RRest=sqrt(zeta1^2+4*zeta3)
Rinfest=(zeta1-RRest)/2
chiest=asin(RRest/sqrt(zeta1^2+zeta2^2+4*zeta3))
SiZCest=2*chiest/pi
qth=2;   % To estimate we need one of the three frequencies
Lam1=-Zy(qth)./((Zx(qth)-Rinfest)*sin(chiest)+Zy(qth)*cos(chiest));
Aoest= Lam1/(RRest*(w(qth)^SiZCest))
plot(Data(:,5),-Data(:,6),'o');hold on
plot(Data(dth,5),-Data(dth,6),'*');    % points used are marked by *
w=2*pi*Data(:,1);    % Impedance is back calculated again
ZZour=Rinfest+RRest./(1+RRest*Aoest*((j*w).^SiZCest));
plot(real(ZZour),-imag(ZZour),':');
xlabel('real part of Z = Z''');ylabel(' imag part of Z =  Z''''')
```

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