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Application of a New Graphical Fitting Approach for Data Analysis in Electrochemical Impedance Spectroscopy

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Abstract- This paper proposes a unique equivalent circuit model of Lithium Bismuth Borate Glass containing 10mol% Nickel and Vanadium ions using LEVM engine by CNLS fitting. A lithium bismuth borate glass framework is processed by the traditional melt quenching method. In this paper considerable effort was put into the development of equivalent circuit model using Impedance Spectroscopy. The result of research revealed that a very good fit circuit is achieved with Admittance parameters.

Keywords- Admittance Spectroscopy (IS), Lithium Bismuth Borate Glass (LBBG), Complex Nonlinear Least Square Fitting (CNLS), Distributed Elements (DEs).

I. INTRODUCTION

Impedance Spectroscopy deals with the complex quantities. IS not only deals with the impedance but four other functions are summed together, thus IS also called as Immittance Spectroscopy.

These four functions are Impedance, Admittance, complex dielectric constant and complex modulus. IS includes the measurement of small signal frequency response of electrolytes, semiconductors, dielectrics and biological cells [1].

In this paper Impedance Spectroscopy is expressed in two forms: Rectangular and Modulus. IS is classified in two categories: Dielectric and Electrochemical Impedance Spectroscopy. These are used in chemical, biochemical and medical research field for analyzing organic compounds [4].

In this paper we use **Lithium Bismuth Borate Glass containing 10mol% Nickel and Vanadium ions for Impedance Spectroscopy Analysis** using CNLS fitting. This glass is developed through melt-quench way[5]. Borate is a standout amongst the most critical glass and has been contained in many sorts of glass frameworks to achieve substance and physical properties. Different dielectric parameters like electrical modulus (M), loss tangent (tanδ), dielectric losses (Ɛ) etc are calculated and their fluctuation with temperature and frequency are analyzed. In this work, an endeavour has been made for the arrangement and portrayal of bismuth-borate glasses with the expansion of lithium oxide as modifier.

1. Complex Nonlinear Least Square (CNLS) fitting: fits complex data to a model. This is the new graphical method for analyzing impedance data presented in the complex plane plot [3]. The point of minimum squares fitting techniques is to locate an arrangement of parameters P which will limit the total:

$$S(P) = \Sigma w_j[Yj - YCj(P)]^2$$

Where the aggregate is assumed control 1.....M, where M is the aggregate number of information focuses, wj is the weight related with the jth point, Yj is the jth information guide an incentive toward be fitted, and YCj (P) is the corresponding value of the calculated fitting function.

The benefits of our access are that it can be utilized effortlessly with generally accessible spreadsheet computation programming like Microsoft Excel [2]. The most imperative preferred standpoint of the CNLS is the likelihood to fit the whole impedance work in the entire scope of frequencies to a model the proportionate circuit.

Ventures for CNLS fitting/recreation:

1.1 FIT: CNLS fitting fits real part, imaginary part and frequency response data of appropriate model.

1.2 GET: Objective parameter estimates, their estimated standard deviation (SD), correlation and SD of fit.

1.3 NO: Subjective graphical, extrapolative and subtractive procedures needed.

1.4 AFTER: fitting, one can analytically separate out the various contributions to the system: electrode effects, Conductive System dispersion data (CSD) response, Dielectric System Dispersion Data (DSD) response and DC conductivity.

II. LEVM/LEVMW TOOL SUMMARY

LEVM is not an acronym but a name. LEVMW is a new window version of LEVM. The early history from claiming LEVM project begins for that paper Eventually Tom's perusing Macdonald Also Garber, j. Electrochemist. Soc. 124 (1977).

The principal adjustment of LEVM were known as LEVM-OLSON or LOMFP, Anyhow clinched alongside 1988 the OLSON and only the fitting system might have been wiped out Also extraordinary and only nonlinear least-squares cycle procedure might have been introduced. The present version is 8.13 was updated in May, 2015. LEVM is powerful measuring tool for CNLS fitting of Impedance Spectroscopic data.

LEVM is a computer program for complex non linear –least squares data fitting, simulation, analysis of high resistivity - disordered materials, glasses, polymers and dielectrics, fits complex, real and imaginary frequency response data. LEVMW includes the entire original LEVM program.

LEVM program includes mainly four functions. First, it might be used to evaluate distribution of relaxation time (DRT) or activation energies (DAE) from frequency or transient response data. It might additionally be utilized for simulation of circuits and different response functions of models and it may be used to fit frequency response or transient response data by complex nonlinear least squares (CNLS) or nonlinear squares (NLS).

Every last one of yield comes about might make plotted over 2-D alternately 3-D type in any immittance level [2]. LEVM bound together bigger number for choices, helping extraordinarily should adaptability and control. It can easily select the fitting models.

LEVM meets expectations straightforwardly with any Windows working framework from W-95 on W-8. LEVM project runs ahead a pc or ms-dos utilizing that Microsoft FORTRAN Power Station v. 1 compiler What's more also aggregated on v. 40 yet the outcomes best run on over specified Windows.

Those introduce rendition from claiming LEVM handles information with a greatest of 2002 information focuses (1001 genuine and 1001 fanciful components) What's more up to 42 allowed parameters. It obliges stretched out memory.

An more diminutive versify about LEVM includes An greatest about 150 focuses Furthermore 28 spare parameters What's more work for standard memory. LEVM gives 37 disseminated unpredictable out components (DCEs alternately DEs). It is likewise utilized will fit information with a suitable reaction model which holds a few temperature subordinate parameters [2].

LEVMW includes LEVMWIN. EXE, a capable fitting motor Furthermore front end realistic interface programs, LEVMRUN. EXE. capable plotting system to LEVMW outputs What's more residuals, Furthermore LEVMVIEW. EXE, and additionally LEVM. HLP.

1. Characteristics of LEVM/LEVMW:

- Capacity to evaluate the parameters of the error variance model, i.e. weighting parameters.
- More than 10 weighting decisions are accessible.
- It estimates the distribution possible by effective strategies for reversal frequency or transient response data.
- Input/output might be in rectangular, polar or log-polar form.
- Greater than 30 different distributed circuit elements (DCEs) are available for different circuits.
- It estimates the parameters of a distribution of relaxation times or activation energies.
- Graphical presentation of spectra, results and parameters is also included.

- MEISP (Multiple EIS parameterization) software package also uses LEVM engine for fitting.
- The fitting and simulation may be carried at immittance level.
- It is also applicable for dielectric, conductive and mixed systems.

2. LEVMW Initialization Steps:

- The input file contains two parts i.e. top part listing the fitting choices and bottom part contains three data columns: frequency, real part, imaginary part (or frequency, magnitude and phase).
- It employs a particular kind of data document for performing CNLS fitting about provided for information.
- The input file assigned which one of the available circuits is suitable for fitting and simulation.
- After selecting fitting circuit initial values must be entered for those free parameters used for fit.
- Data are input in LEVM in the form of impedance, admittance, modulus and dielectric constant or complex capacitance.

3. Input File:

MKLIO combines the top part of LEVM input file with arbitrary data file to produce a new complete input file. A finish data document incorporates a header and the following that an information segment. Those headers a component obliges that a number for decisions be constructed and assessed qualities from claiming nothing and settled parameters.

Two main points while preparing input file are: a) You must choose appropriate fitting model from possible circuits and b) Information must be joined with LEVM input header document to make completely executable information record.

4. Graphics Information:

A very useful addition to LEVM is the 2-D and 3-D plotting program. Its result are coloured and carries all necessary data transformation and even rotate 3-D plots if required [2].

Another 2-Dimensional alternative has been included to permit the plotting of the absolute value of the tangent of the data (only in rectangular form) (OTN) or its inverse (ITN). CPTRAN (FORTRAN) program is used to plot the data and represent the results with the help of graphs.

5. Output Files:

LEVM produces screen yield throughout operation this will be inadequate and the primary yield seems in the files are AUXPNTL and PNTOUTL.

After observing above files the two standard deviations, S_F: PRSDAV (weighting residuals) and PRSDRMS (relative residuals) are automatically induced at the end of the third line of OUTIN and if they exceed 0.2 or 0.3, it is a poor fit. For a good fit, one would expect 0.03 or less. A fit quality factor (FQF) value is also given to help in comparing two fits [2].

- **AUXPNTL** is for auxiliary output and allows user to convert data between 16 different modes. It is a secondary output file which contains list of parameter inputs and includes a list of the data , the fitted results, and the fitting residuals of each point[2].
- **PNTOUTL** is used for main output printing. The PNTOUTL file is obtained by running AZC. You will need to first find the circuit model used (**hereB**) and then use the identification list for this circuit in order to pair the parameter values with the actual elements in the B circuit used in the fitting (i.e. know non-zero parameters in the PNTOUTL starting listing). Just parameter qualities with a 1 or 2 following them would free throughout the fitting. Those more spare parameters on a fit a greater amount alluring those fit that their starting esteem may be near their last converged qualities. LEVM can converge when parameter estimates are far from their correct values, the more free parameters in the fitting; the more difficult it is for the program to converge to the correct set of parameter estimates.

III. PROPOSED WORK

There are five major steps in the proposed work of our research:

- Data Collection
- Input File Preparation
- Pre- Analysis
- Resetting of parameters
- Equivalent Circuit Model

1. Data Collection:

The first step of our analysis is to collect the datasheet of Lithium Bismuth Borate Glass parameters.

There are many discrete elements available designed to be use in Immittance Spectroscopy. These discrete elements are resistance, capacitance, inductance, modulus, relaxation time constant, dielectric constant etc but here mainly we use Resistance and Capacitance parameters for our work.

These parameters may be free or fixed fitting parameters. The impedance spectroscopy of our dielectric glass is carried out at temperature of 322 K and frequency range of 1MHz-5MHz. This datasheet was provided by Physics Department which is shown in fig.1.

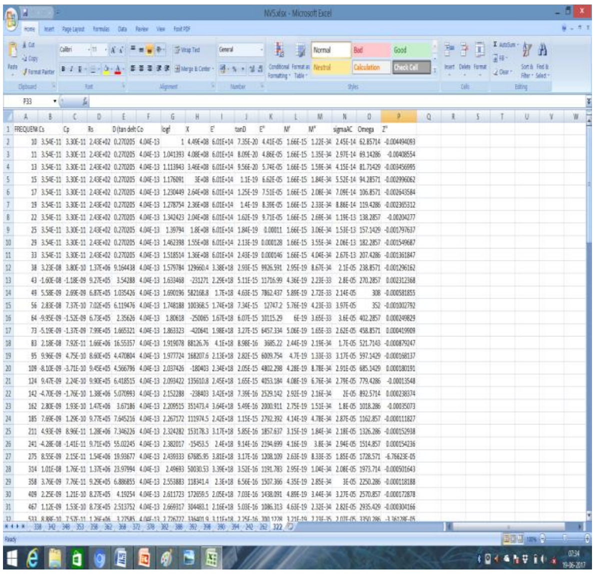


Fig 1. Datasheet of LBBG.

2. Input File Preparation:

To fit our own data to a model we have to choose proper one, get ready the top part of an input file and consolidated it with our bottom part of file which contains the information to create the last LEVM input file.

Our information should be organized in three columns: frequency, real part, imaginary part and if the imaginary part of the data is positive, it is changed to negative in the final output file as shown in fig.1. In input file preparation we need to determine which model parameters should be free or fixed.

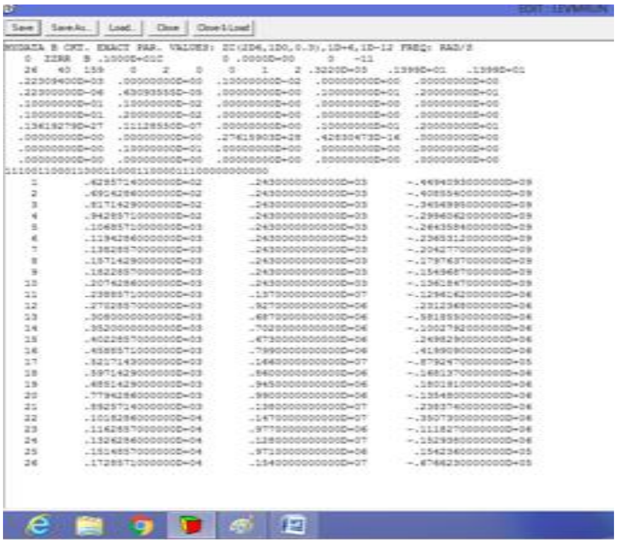


Fig 2. Prepared Input File.

3. Pre Analysis:

At this level, the output obtained as a result of the initial guesses of the parameters values in the top part of the input file is determined. The quantities, PRSDAV and PRSDRMS are expected to be 0.03 or less for a good fit otherwise it is not a good fit.

4. Resetting of Parameters:

Values of standard deviations are automatically induced at the end of OUTIN line. If these values be less than or equal to 0.03 than no need to change the parameters values otherwise we need to change the values of fixed or free parameters in ADVANCED EDITOR section.

5. Equivalent Circuit Determination:

After performing above steps we have to select the best fit circuit from circuits A, B, C up to T. Here we determine the circuit B equivalent circuit because values of PDAV and PDRMS is less than 0.03.In the equivalent circuit DE represents the distributed/ discrete elements which may be in series or parallel combination.

IV. RESULTS

Furthermore screen output, several output files are produced by normal frequency response. The most significant is shown in fig.3 i.e.

PNTOUTL file which shows the values of two standard deviations less than 0.03 these values are 2.8786D-02 and 1.8838D-02 which shows that circuit we select is good fit and equivalent circuit of this model is shown in fig.6.

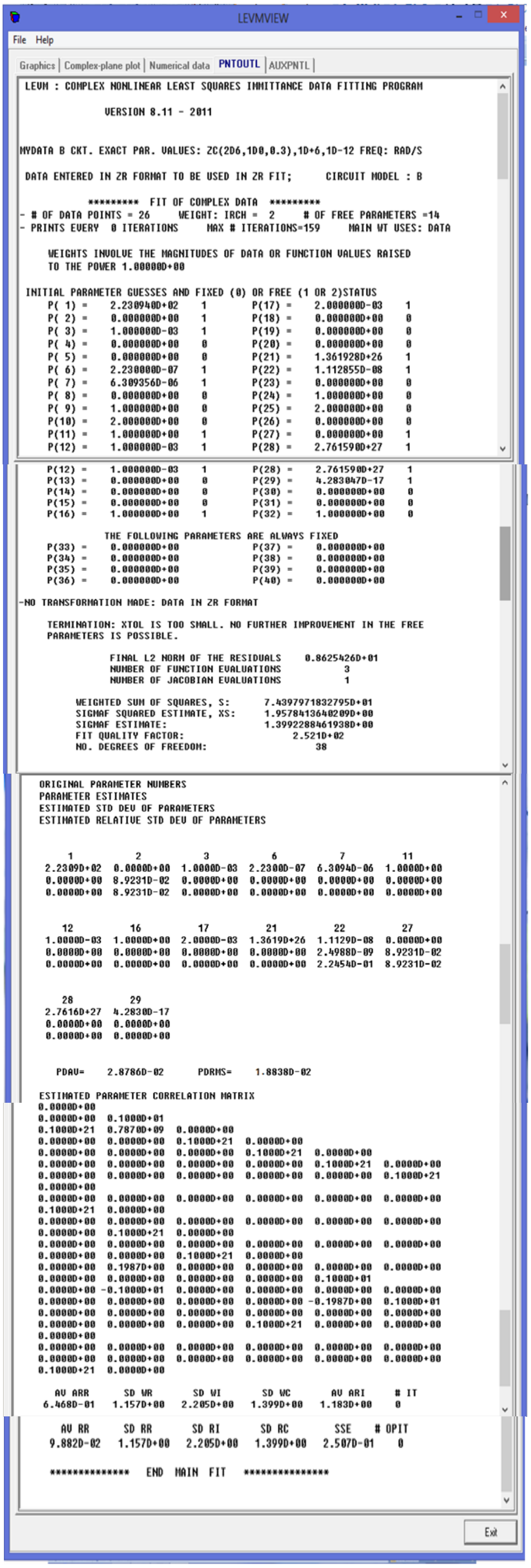


Fig 3. PNTOUTL File.

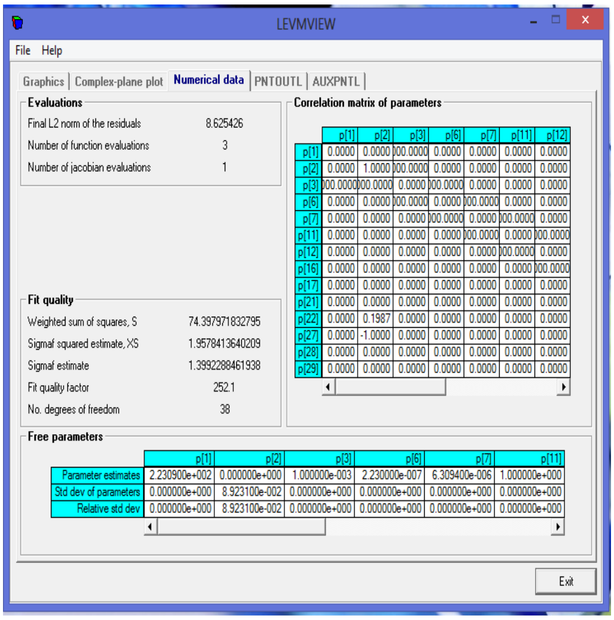
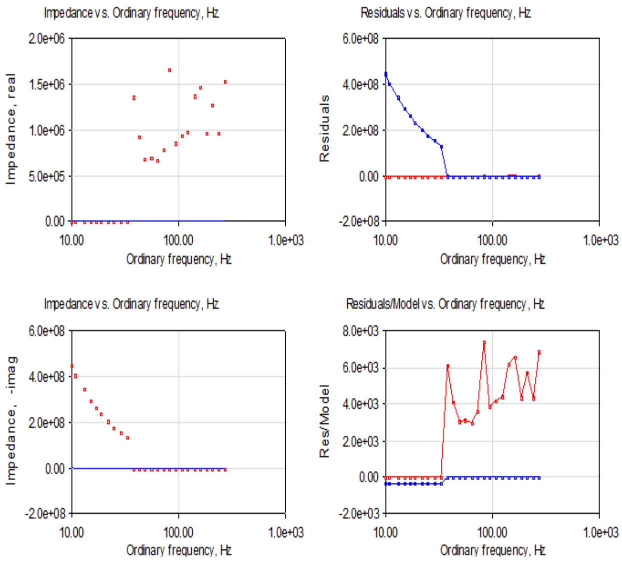


Fig 4. Numerical Data File.

Fig. 4 shows the correlation matrix of parameters and the free parameters variations i.e. standard deviation with Fit Quality Factor (FQF).



(a) (b)

Fig 5. a) Impedance v/s frequency curve of LBBG at 322°K and b) Residuals v/s frequency curve for LBBG at 322°K.S.

Fig.5 shows direct graphical output obtained from LEVMW CNLS fitting of the material used at temp. 322°K. The left two plots show the input data as dots and fitting result as solid lines.

The right two plots show the real part residuals and relative residuals by red lines and imaginary part by blue lines.

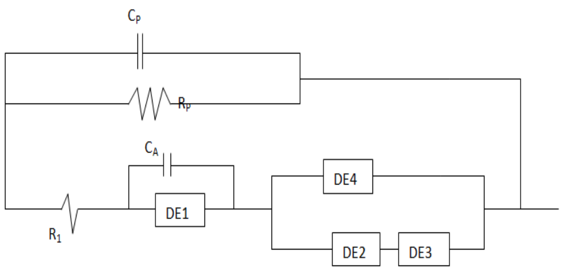


Fig 6. Proposed Equivalent Circuit Model.

Fig.6 shows the equivalent circuit model of LBBG at temperature of 322°K. Here, 4 distributed elements are connected in series as well as parallel combinations. These DEs are RDE, UDE, TDE, NDE, and PDE. The changes allow us to better circuit elements.

IV. CONCLUSION

This paper deals with the designing of equivalent circuit model for Lithium Bismuth Borate Glass based on the impedance spectroscopic data, the circuit mode, fitting circuit choices made in the input file and the parameter values assigned in the input file.

A new accurate method of determining equivalent circuit of dielectric material using CNLS fitting. The circuit is very simpler using a pattern: Any element is not present is set to zero. Future scope of this research work is to measure the larger signal frequency response of semiconductors, electrolytes.

We should make the measurement of the same material at same temperature using two or more electrodes. Other quantities like light, magnetic field can be used for further analysis .In future we add further weighting choices to least squares to minimize the sum of theabsolute values of the residuals.

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