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(54) **METHOD AND APPARATUS FOR
DETECTING CELL DETERIORATION IN AN
ELECTROCHEMICAL CELL OR BATTERY**

(57) **ABSTRACT**

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MN (US)**

A testing device detects and quantifies cell deterioration of an electrochemical cell or battery. The device contains measuring circuitry adapted to apply time-varying electrical excitation to said cell or battery, to sense time-varying electrical response to said excitation, and to utilize said excitation and response to determine components of complex immittance (i.e., either impedance or admittance) at $n+m$ discrete frequencies, where n is an integer equal to or greater than two and m is an integer equal to or greater than one. Computation circuitry utilizes measured complex immittance components at the n discrete frequencies to evaluate the elements of a $2n$ -element equivalent circuit model. It then calculates the complex immittance of this model at the m discrete frequencies and mathematically compares components of the calculated immittances with components of the measured immittances at the m discrete frequencies. The results of this comparison are related to the degree of cell deterioration. A pass/fail determination can thus be made based solely upon cell deterioration—without even knowing the battery's manufacturer, group size, or its electrical ratings.

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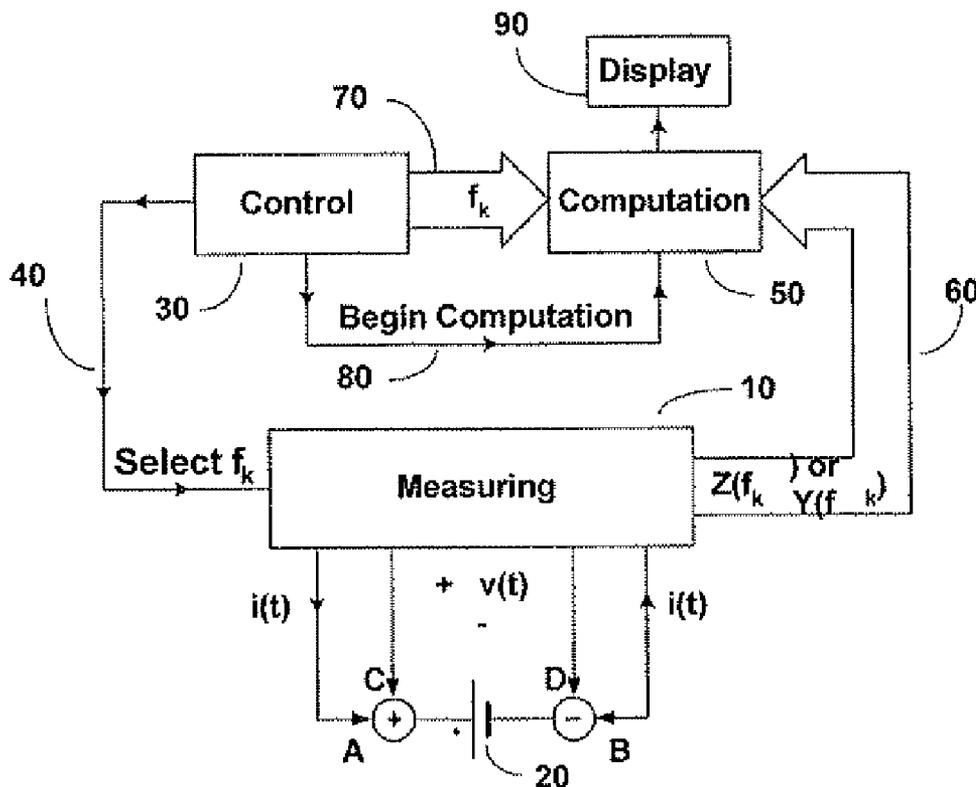


Fig. 1

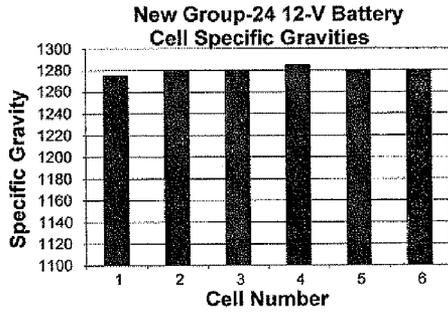


Fig. 2

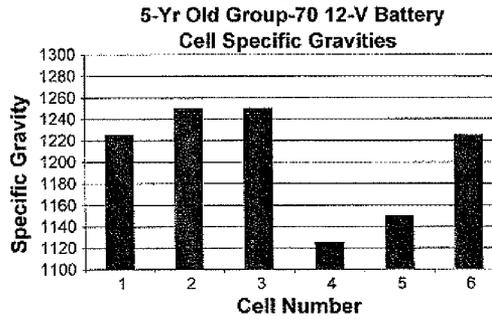


Fig. 3

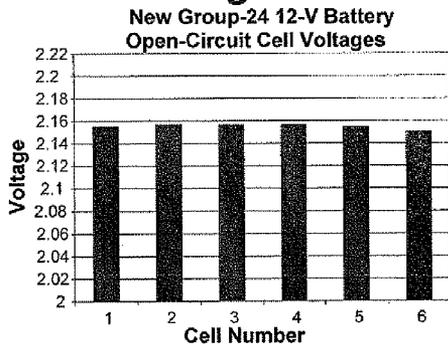


Fig. 4

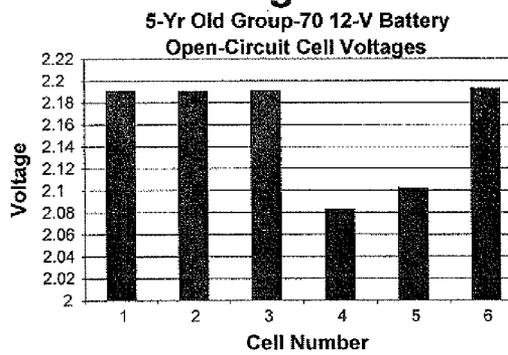


Fig. 5

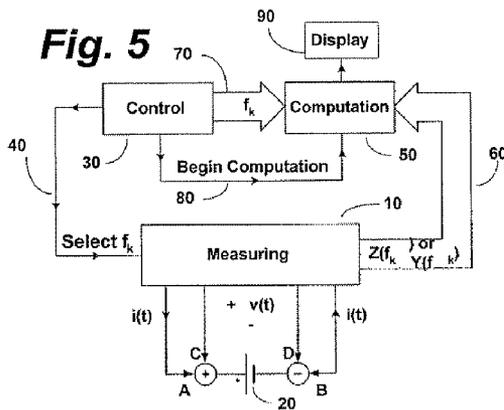


Fig. 6

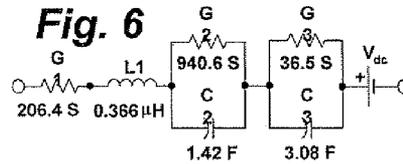


Fig. 7

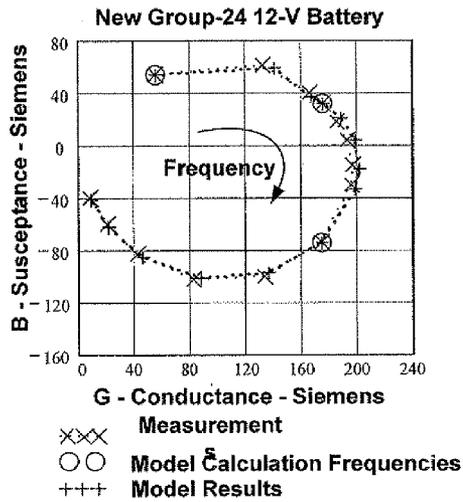


Fig. 8

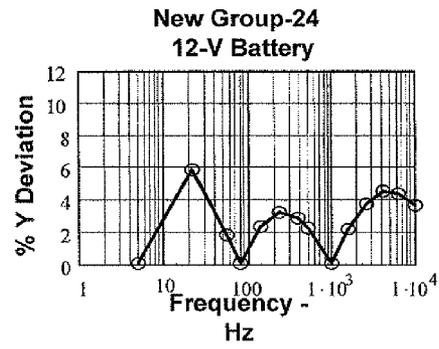


Fig. 9

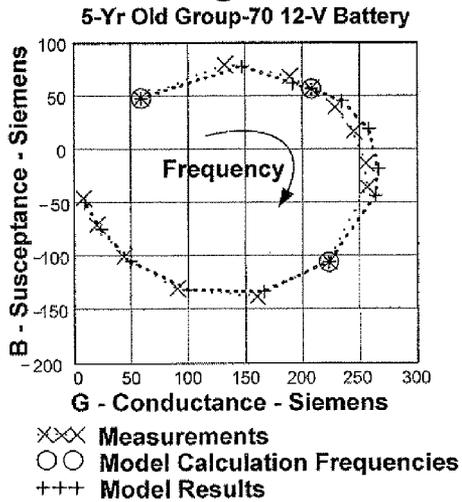
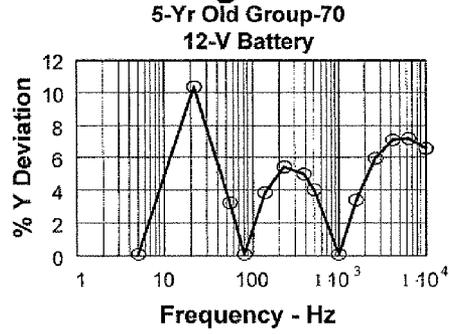


Fig. 10



METHOD AND APPARATUS FOR DETECTING CELL DETERIORATION IN AN ELECTROCHEMICAL CELL OR BATTERY

BACKGROUND OF THE INVENTION

[0001] Batteries comprising a plurality of series-connected electrochemical cells are ubiquitous in transportation and industrial applications. Six-cell lead-acid batteries are commonly used for engine starting and energy storage in conventional automobiles and trucks and for energy storage in standby applications. Batteries comprising larger arrays of lithium-ion and nickel-metal-hydride cells are becoming increasingly common in hybrid and all-electric vehicles. With all such batteries, the cells have maximum capability and their properties are relatively uniformly distributed over the battery when the battery is new. As the battery ages, however, the cells deteriorate and their properties become more non-uniformly distributed. The challenge is to detect and quantify such deterioration in order to ascertain when the battery should be replaced.

[0002] In the past, lead-acid batteries always had filler caps making the electrolytes of the individual cells accessible. A strategy for detecting cell deterioration in such batteries employed a hydrometer to observe the distribution of the specific gravity values among the cells. A distribution that was sufficiently nonuniform identified a battery that should be replaced. For example, the following information can be found on the Interstate Battery website: "Check each individual battery cell. If the specific gravity varies more than 0.050 or "50 points" among the cells while the battery is at a 75% state of charge or above, then the battery is bad and should be replaced." Unfortunately, this strategy has little value today since cell electrolytes are never accessible in AGM batteries and often not even accessible in flooded batteries.

[0003] Another earlier strategy for detecting a nonuniform distribution of cell properties was popular when the battery's inter-cell connectors were exposed. With such batteries, one could measure and compare the individual cell voltages. Cell voltages that deviated sufficiently from the average value identified a battery that should be replaced. Passing current through the battery while observing cell voltages enhanced the effect. Today, however, inter-cell connectors are not exposed, thus rendering this strategy also of little value.

[0004] Clearly, a method and apparatus that detects and quantifies cell deterioration in batteries for which neither cell electrolytes nor cell voltages are available would be desirable. The present invention addresses this need. It is based upon the important discovery that a well-known electrical circuit model best describes the battery's immittance characteristics (i.e., impedance or admittance characteristics) when the battery is new and all of its cells have nearly identical electrical properties. As the battery ages, cell deterioration sets in causing the cells' electrical properties to deviate from the norm and from one another. This deterioration can be detected and quantified by observing how well the circuit model actually "fits" the deteriorated battery. That is, how well the model predicts the battery's actual immittance at a particular measurement frequency. One advantage of this technique is that a pass/fail determination can be made without needing to know the battery's manufacturer, group size, or its electrical ratings.

SUMMARY OF THE INVENTION

[0005] A testing device detects and quantifies cell deterioration of an electrochemical cell or battery. The device con-

tains measuring circuitry adapted to apply time-varying electrical excitation to said cell or battery, to sense time-varying electrical response to said excitation, and to utilize said excitation and response to determine components of complex immittance (i.e., either impedance or admittance) at $n+m$ discrete frequencies, where n is an integer equal to or greater than two and m is an integer equal to or greater than one. Computation circuitry utilizes measured complex immittance components at the n discrete frequencies to evaluate the elements of a $2n$ -element equivalent circuit model. It then calculates the complex immittance of this model at the m discrete frequencies and mathematically compares components of the calculated immittances with components of the measured immittances at the m discrete frequencies. The results of this comparison are related to the degree of cell deterioration. A pass/fail determination can thus be made based solely upon cell deterioration—without even knowing the battery's manufacturer, group size, or its electrical ratings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] FIG. 1 is a bar graph depicting the electrolyte specific gravities of the individual cells of a new Group-24 12-volt automotive battery that is fully charged.

[0007] FIG. 2 is a bar graph depicting the electrolyte specific gravities of the individual cells of a 5-year old Group-70 12-volt automotive battery that is fully charged.

[0008] FIG. 3 is a bar graph depicting the open-circuit voltages of the individual cells of the fully-charged new Group-24 12-volt automotive battery.

[0009] FIG. 4 is a bar graph depicting the open-circuit voltages of the individual cells of the fully-charged 5-year old Group-70 12-volt automotive battery.

[0010] FIG. 5 is a block diagram of a device for detecting and quantifying cell deterioration in an electrochemical cell or battery according to the present invention.

[0011] FIG. 6 depicts a six-element ($n=3$) equivalent circuit representation of the new fully-charged Group-24 12-volt automotive storage battery.

[0012] FIG. 7 is a Nyquist plot representation of the complex admittance of the new fully-charged Group-24 12-volt automotive storage battery modeled in FIG. 6. Both measured and model-derived admittance values are plotted. The circled data points identify the three frequencies (5, 80, 1000 Hz) used for model evaluation.

[0013] FIG. 8 is a plot of the percentage admittance deviation between measured and calculated values of FIG. 7.

[0014] FIG. 9 is a Nyquist plot representation of the complex admittance of the fully-charged 5-year old Group-70 12-volt automotive battery. Both measured and model-derived admittance values are plotted. The circled data points identify the three frequencies (5, 80, 1000 Hz) used for model evaluation.

[0015] FIG. 10 is a plot of the percentage admittance deviation between measured and calculated values of FIG. 9.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0016] FIG. 1 is a bar graph disclosing specific gravities of the individual cells of a battery having very little cell deterioration. This battery is a brand-new Exide Dura-Start Group-24 12-volt automotive battery rated 525 CCA. It was fully charged. This battery possessed filler caps, so the cell electrolytes were readily accessible. One sees that the maximum

gravity difference occurred between cells 1 and 4 and was only 10 points. That is well within the 50 point criterion allowed by the testing procedure described above. Thus, this battery would be considered “good” and could be returned to service.

[0017] FIG. 2 is a bar graph disclosing specific gravities of the individual cells of a battery having cell deterioration. This battery is a 5-year old AC Delco Group-70 12-volt automotive battery rated 770 CCA. It too was fully charged. Since this battery did not have filler caps, it was necessary to physically cut the top off of the battery to gain access to the electrolytes. One sees a maximum gravity difference of 125 points between either cell 2 or cell 3 and cell 4. This result is outside of the 50 point criterion permitted by the testing procedure described above. Furthermore, cell 5 deviated by 100 points from either cell 2 or cell 3 and was therefore also out of tolerance. Thus, on the basis of cell deterioration, this battery should be removed from service.

[0018] FIGS. 3 and 4 are bar graphs showing the open-circuit cell voltages for these same two batteries measured at the inter-cell connectors. In order to gain access to these connectors on the new Group-24 battery, it was necessary to cut the top off of this battery as well. FIG. 3 shows that the maximum voltage difference between cells of the new battery occurred between cells 4 and 6 and was only 0.0066 volts. On the other hand, the 5-year old battery had differences of 0.1099 volts between cells 4 and 6, and of 0.0909 volts between cells 5 and 6. These results are completely consistent with the specific gravity differences disclosed in FIGS. 1 and 2 and again illustrate cell deterioration in the 5-year old battery—but not in the new battery.

[0019] The data disclosed in FIGS. 1 through 4 are very revealing vis-à-vis cell deterioration. Unfortunately, most of these data would be unavailable to an investigator interested in field-testing batteries.

[0020] FIG. 5 discloses a block diagram of apparatus for detecting and quantifying cell deterioration without requiring access to cell electrolytes or inter-cell connectors. It is based upon techniques disclosed previously in U.S. Pat. Nos. 6,002, 238, 6,172,483, 6,262,563, and 6,294,896. Measuring circuitry 10 electrically couples to cell/battery 20 by means of current-carrying contacts A and B and voltage-sensing contacts C and D. Measuring circuitry 10 passes a periodic time-varying current $i(t)$ through contacts A and B and senses a periodic time-varying voltage $v(t)$ across contacts C and D. By appropriately processing and combining $i(t)$ and $v(t)$, measuring circuitry 10 determines real and imaginary parts of complex immittance, either impedance Z or admittance Y, at a measuring frequency f_k ; where f_k is a discrete frequency contained in the periodic waveforms of both $i(t)$ and $v(t)$.

[0021] Control circuitry 30 couples to measuring circuitry 10 via command path 40 and commands measuring circuitry 10 to determine the complex immittance of cell/battery 20 at each one of n+m discrete measuring frequencies, where n is an integer number equal to or greater than two and m is an integer number equal to or greater than one. This action defines 3(n+m) experimental quantities: the values of the n+m measuring frequencies and the values of the n+m imaginary parts and n+m real parts of the complex parameter at the n+m measuring frequencies.

[0022] Computation circuitry 50 couples to measuring circuitry 10 and to control circuitry 30 via data paths 60 and 70, respectively, and accepts the 2(n+m) experimental values from measuring circuitry 10 and the values of the n+m mea-

suring frequencies from control circuitry 30. Upon a “Begin Computation” command from control circuitry 30 via command path 80, computation circuitry 50 uses algorithms disclosed in U.S. Pat. Nos. 6,037,777 and 6,222,369 to combine these 3n quantities numerically to evaluate the 2n elements of an equivalent circuit model of the cell/battery. Computation circuitry 50 then calculates the complex immittance of this model at the m discrete measurement frequencies and mathematically compares components of these calculated immittances with components of the measured immittances at the m discrete frequencies. Cell deterioration is identified by the results of this comparison. If desired, computation circuitry 50 can make a pass/fail determination and can output this comparison result to the user on display 90.

[0023] In practice, a microprocessor or microcontroller running an appropriate software program can perform the functions of both control circuitry 30 and computation circuitry 50.

[0024] FIG. 6 discloses a six-element equivalent circuit model of the new fully-charged Group-24 automotive battery depicted in FIGS. 1 and 3. This circuit model was evaluated using apparatus of the type disclosed in FIG. 5 with n=3. The three measurement frequencies were 5 Hz, 80 Hz, and 1000 Hz.

[0025] FIG. 7 shows a Nyquist admittance plot for the battery whose model is depicted in FIG. 6 at 14 discrete measurement frequencies (n+m=14) ranging from 5 Hz to 10,000 Hz.

[0026] Admittance Y is a complex quantity

$$Y = G + jB \tag{1}$$

in which the real component G is conductance and the imaginary component B is susceptance. Complex admittance Y is the reciprocal of complex impedance

$$Z = 1/Y = R + jX \tag{2}$$

The real component of Z is resistance R and the imaginary component is reactance X.

[0027] The Nyquist admittance plot of FIG. 7 is a plot of susceptance B versus conductance G with frequency as the common parameter. As shown in FIG. 7, the data curves proceed clockwise as frequency increases from 5 to 1000 Hz. Both the 14 experimental data points and the 14 data points calculated from the model of FIG. 6 are displayed in FIG. 7. Data at the three frequencies used to evaluate the model (5, 80, and 1000 Hz) are identified by circles. As expected, measured and calculated data agree exactly at these three frequencies. At all 11 of the other measurement frequencies, comparisons show that the measured and calculated data disagree slightly.

[0028] To more carefully compare measured and calculated data, I define the Percentage Y Deviation as follows:

$$\% Y \text{ Deviation} = \frac{\{(G_{meas} - G_{calc})^2 + (B_{meas} - B_{calc})^2\}^{1/2}}{|Y|} \times 100 \tag{3}$$

A plot of % Y Deviation as a function of frequency at the 14 measurement frequencies is shown in FIG. 8. One sees that the % Y Deviation is zero at the three modeling frequencies, 5, 80, and 1000 Hz. At all 11 other frequencies, the % Y Deviation is positive and attains its maximum value of 5.9 at f=22 Hz. Note the lack of scatter in the data of FIG. 8. This is a strong indication of very high measurement precision.

[0029] The apparatus of FIG. 5 was employed to measure the complex admittance of the 5-year old Group-70 battery at the same 14 discrete measurement frequencies ($n+m=14$) used previously. FIG. 9 is a Nyquist admittance plot displaying the results of those measurements. Again, the data curves proceed clockwise as frequency increases. Both the 14 experimental data points and the 14 data points calculated from the 6-element circuit model are displayed in FIG. 9. Again, data at the three frequencies used to evaluate the model (5, 80, and 1000 Hz) are identified by circles. Measured and calculated data again agree exactly at these three frequencies. At all 11 other frequencies, comparisons again show that measured and calculated data disagree. However, the disagreement is larger for the 5-year old Group-70 battery than that shown in FIG. 7 for the new Group-24 battery.

[0030] FIG. 10 displays a plot of % Y Deviation for the 5-year old Group-70 battery at the 14 measurement frequencies displayed in FIG. 9. One again sees that the % Y Deviation is zero at the three modeling frequencies, 5, 80, and 1000 Hz. At all 11 other frequencies, the % Y Deviation is positive and attains its maximum value of 10.5 at $f=22$ Hz. Again note the complete lack of scatter in the data. This is again a strong indication of very high measurement precision.

[0031] By comparing FIGS. 8 and 10, one sees that an increase in cell deterioration is associated with increases in % Y Deviation at every one of the $m=11$ measurement frequencies not used in the model evaluation. Accordingly, values of % Y Deviation at selected frequencies can be advantageously utilized to identify and quantify the degree of cell deterioration in the battery—without requiring access to either cell electrolytes or cell voltages. One need only determine % Y Deviation at, say, one “extra” frequency ($m=1$) in order to apply this principle. For example, the % Y Deviation at 22 Hz could be used alone. This quantity is seen to be nearly twice as large (10.5) for the 5-year old battery having significant cell deterioration than for the brand-new battery (5.9) having very little cell deterioration. On the basis of this number, a pass/fail determination could be made without knowledge of the battery’s manufacturer, group size, or electrical ratings.

[0032] This completes the disclosure of my invention. Although, for illustrative purposes, measurements on only two batteries have been disclosed above, I have found the results to be generally true across a wide spectrum of batteries. Measurements on other batteries from different manufacturers, of different group sizes, and having different electrical ratings have all corroborated the results described herein. That is one significant advantage of this technique. One need not know the battery’s electrical ratings or even its group size or manufacturer in order to make a pass/fail determination based upon cell deterioration.

[0033] I have also found that other battery properties such as state-of-charge can be determined by measuring “Percentage Y Deviation” of batteries that are known to have little cell deterioration. Although the “Percentage Y Deviation” defined by equation (3) was introduced to mathematically compare measured and calculated admittance components, other mathematical methods and comparison quantities are possible. For example, I have found that the “Percentage Z deviation”, defined in terms of measured and calculated Z components (R and X), gives identical results. Furthermore, one could make mathematical comparisons in other ways or by using any of the single admittance components R, X, G, or B. One could also use other battery models or other values of n and m . I have found that $n=4$ also works very well. Workers

skilled in the art will recognize that these and other variations may be made in form and detail without departing from the true spirit and scope of my invention.

What is claimed is:

1. Apparatus for determining a physical property of an electrochemical cell or battery comprising:

measuring circuitry adapted to apply time-varying electrical excitation to said cell or battery, to sense time-varying electrical response to said excitation, and to utilize said excitation and said response to determine components of complex admittance at $n+m$ discrete frequencies, where n is an integer equal to or greater than two and m is an integer equal to or greater than one;

computation circuitry responsive to said complex admittance components and adapted to evaluate the elements of a $2n$ -element equivalent circuit model from said complex admittance components at said n discrete frequencies, adapted to calculate the complex admittance components of said model at said m discrete frequencies, and adapted to mathematically compare said calculated components with said measured admittance components at said m discrete frequencies, the results of said comparison being related to said physical property.

2. The apparatus of claim 1 including display circuitry responsive to said computation circuitry and adapted to communicate results of said comparison to a user.

3. The apparatus of claim 1 wherein said physical property is the degree of cell deterioration of said electrochemical cell or battery.

4. The apparatus of claims 2 and 3 wherein said results comprise a pass/fail determination.

5. The apparatus of claim 1 wherein said physical property is the state-of-charge of said electrochemical cell or battery.

6. The apparatus of claim 1 wherein n is equal to three and m is equal to one.

7. The apparatus of claim 1 wherein said complex admittance comprises complex admittance and said mathematical comparison comprises computing the percentage Y deviation between measured and calculated real and imaginary components of said complex admittance.

8. The apparatus of claim 1 wherein said complex admittance comprises complex impedance and said mathematical comparison comprises computing the percentage Z deviation between measured and calculated real and imaginary components of said complex impedance.

9. A method for determining a physical property of an electrochemical cell or battery comprising the steps of:

measuring the complex admittance of said cell or battery at $n+m$ discrete frequencies where n is an integer equal to or greater than two and m is an integer equal to or greater than one;

evaluating elements of an equivalent circuit model from said admittance at said n discrete frequencies, said model comprising $2n$ discrete electrical elements;

calculating the complex admittance of said circuit model at said m discrete frequencies;

mathematically comparing components of said calculated and measured complex admittances at said m discrete frequencies; and,

determining said physical property from said comparison.

10. The method of claim 9 wherein said physical property is the degree of cell deterioration of said electrochemical cell or battery.

11. The method of claim 10 including communicating a pass/fail determination to a user based upon said degree of cell deterioration.

12. The method of claim 9 wherein said physical property is the state-of-charge of said electrochemical cell or battery.

13. The method of claim 9 wherein n is equal to three and m is equal to one.

14. The method of claim 9 wherein said complex immittance comprises complex admittance and said mathematical comparison comprises computing the percentage Y deviation between measured and calculated real and imaginary components of said complex admittance.

15. The method of claim 9 wherein said complex immittance comprises complex impedance and said mathematical comparison comprises computing the percentage Z deviation between measured and calculated real and imaginary components of said complex impedance.

16. Apparatus for evaluating the degree of cell deterioration in an electrochemical cell or battery comprising:

electrical excitation circuitry adapted to apply time-varying electrical excitation to said cell or battery, said excitation containing frequency components at n+m discrete frequencies where n is an integer equal to or greater than two and m is an integer equal to or greater than one;

response sensing circuitry configured to sense time-varying electrical response of said cell or battery at said n+m discrete frequencies;

computation circuitry responsive to said time-varying excitation and to said time-varying response and adapted to compute the complex immittance of said cell or battery at said n+m discrete frequencies, adapted to evaluate element values of a 2n-element equivalent circuit model of said cell or battery from said n immittance values, adapted to calculate complex immittance components of said model at said m discrete frequencies, and adapted to mathematically compare said calculated components with said measured immittance components at said m discrete frequencies, the results of said comparison being related to said degree of cell deterioration.

17. The apparatus of claim 16 including display circuitry responsive to said computation circuitry and adapted to communicate results of said comparison to a user.

18. The apparatus of claim 17 wherein said results comprises a pass/fail determination.

19. The apparatus of claim 16 wherein n is equal to three and m is equal to one.

20. The apparatus of claim 16 wherein said complex immittance comprises complex admittance and said mathematical comparison comprises computing the percentage Y deviation between measured and calculated real and imaginary components of said complex admittance.

21. The apparatus of claim 16 wherein said complex immittance comprises complex impedance and said mathematical comparison comprises computing the percentage Z deviation between measured and calculated real and imaginary components of said complex impedance.

22. A method for determining the degree of cell deterioration of an electrochemical cell or battery comprising the steps of:

measuring the complex immittance of said cell or battery at n+m discrete frequencies where n is an integer equal to or greater than two and m is an integer equal to or greater than one;

evaluating elements of an equivalent circuit model from said n immittance measurements, said model comprising 2n discrete electrical elements;

calculating the complex immittance of said circuit model at said m discrete frequencies;

mathematically comparing components of said calculated and measured complex immittance at said m discrete frequencies; and,

determining said degree of cell deterioration from said comparison.

23. The method of claim 22 wherein n is equal to three and m is equal to one.

24. The method of claim 22 wherein said complex immittance comprises complex admittance and said mathematical comparison comprises computing the percentage Y deviation between measured and calculated real and imaginary components of said complex admittance.

25. The method of claim 22 wherein said complex immittance comprises complex impedance and said mathematical comparison comprises computing the percentage Z deviation between measured and calculated real and imaginary components of said complex impedance.

26. The method of claim 22 including communicating a pass/fail determination to a user based upon said degree of cell deterioration.

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