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A Comprehensive Method to Characterize Mixed Conduction Electrolytes

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1. Introduction

In a very broad sense, nearly every material is a mixed conductor. The extent of ionic or electronic transport may be extremely limited in a particular sample, but it does exist. The relative amounts of ionic and electronic transport determine the usefulness of a solid electrolyte. When attempting to improve an electrolyte system, it is vital to determine how all of the transport properties change. This both determines whether a specific change has the desired effects and aids in formulating a theoretical explanation for the phenomena. In this paper we will describe the design and operation of an automated measuring system to characterize the electrical behaviors of high resistance mixed conductors.

2. Background

ac impedance spectroscopy is a powerful technique to probe an electrolyte. The phase shifts, produced by the sample electrolyte in an ac signal fed into the sample, reveal details of the electrical properties. The relationship of these phase shift to the frequency of the ac signal can be related to an electrical model of the sample [1]. Parameters normally obtained by impedance spectroscopy include interface capacitance, bulk capacitance, ionic and electronic conductivities and diffusivities as well as the relationship between these electrical elements. One problem with relying on ac impedance spectroscopy as the sole method of characterizing an electrolyte is that most electrolyte applications are dc in nature. This can limit the applicability of the ac data to practical performance parameters. In order to obtain the equivalent range of information with dc as with ac it is necessary to use a polarization method [2]. Using a Wagner cell arrangement with a blocking electrode, the interface capacitance, bulk capacitance, and diffusivities are revealed through relaxation studies [3]. The electronic conductivity is separated by the steady state current-potential behavior.

3. Requirements

In both ac and dc systems, both the current through and the voltage across the sample must be monitored. Ideally, the monitoring is continuous to detect the phase shifts in the ac work and accurately describe the relaxation events in dc. If changes in sample temperature are controlled and monitored, the temperature dependence of the various parameters can be determined. This allows conformation of the relationship between the ac and dc results. The use of multiple samples and some means of accurately switching the monitoring between samples is required to confirm significance and validity of the data.

Specific to de polarization, the system must be capable of accurately reintroducing instantaneous steps in the polarizing potential and both the beginning and ending levels must be stable. A range of these stable polarizing potentials is necessary to determine the steady state current-potential behavior.

In ac impedance spectroscopy, the ac source signal must maintain a range of stable frequencies. Furthermore, the potential and current monitors should follow these frequency changes. The current-potential monitors are also responsible for determining their relative phase shifts and magnitude, in other words, the complex impedance.

4. Equipment

To meet these requirements, the authors use a Data General NOVA III computer and associated equipment. The NOVA computer employs a flexible bus architecture that enables easy

expansion and customizing of the system. As currently configured, the NOVA supports 64KB main memory, a CRT terminal, a hard copy terminal, a plotter, two 300KB floppy disk drives, two 10MB hard disk drives, a digital interface unit, a real time clock, and a data acquisition and control unit.

The digital interface unit provides two independent banks of ten switches, one switch "oil" per bank, and an IEEE-488 communications bus. This interface was custom designed. Its logic diagram is given in fig. 1. The data acquisition and control unit is a microprocessor controlled assembly that removes all overhead processing from the NOVA. It controls four 5 V, 12 bit bipolar digital to analog (D/A) converters and a 16 channel, programmable gain multiplexor feeding a 5 V, 12 bit differential analog to digital (A/D) converter. The real time clock enables accurate timing of events on a one second time scale.

Using this NOVA system, an automated ac/dc measurement system has been designed. External equipment consists of: a digitally controlled switching unit, an isolation amplifier, a thermocouple amplifier, a Research Incorporated 6101 temperature controller and 623 power regulator connected to a Marshall tube furnace, and an EG&G PAR 5206 lock-in-amplifier (LIA). The block diagram for ac/dc portion of the system is shown in fig. 2. In converting to the ac system only a few changes need to be made. The Power line from the D/A unit to the switch box is replaced with the output signal from the LIA. Also the current and voltage lines from the switch box to the isolation amplifier are now connected to the input and reference signals of the LIA respectively. The LIA is connected to the NOVA via IEEE-488 bus.

The switch box is a custom designated unit capable of switching the current and voltage sensing circuits into any one of six different sample circuits. It is also capable of removing the polarizing potential from any circuit for open circuit measurements. All switches are digitally controlled mercury relays capable of handling currents in the range of 1A to 1nA reliably. The switching time for this unit is less than 5 ms. The measuring and sample circuitry of this unit is given in fig. 3. The switching control circuits for each set of relays are given in fig. 4. Switches 1 and 2 in fig. 3 are actually six separate DPDT relays (fig. 4a) while switches 3, 4 and 5 are twelve paired DPDT relays (fig. 4b).

The isolation amplifier is required to prevent the active polling procedure of the NOVA's A/D unit from disturbing the samples. This is accomplished by feeding the current and voltage signals from the switch box into two differential instrumentation amplifiers. The amplifiers' output then lead to the A/D unit. The current amplifier has four manually selectable gains (1, 10, 100, 1000) to increase its range of operation. The current amplifier uses an inter-changeable viewing resistor to convert from a current to a voltage upon which the amplifier acts. The inter-changability allows the selection of the current range appropriate to the samples. The circuit diagram for this unit is given in fig. 5. The thermocouple amplifier has essentially the same design. However, since the use of the temperature is different than the use of the current-voltage information, a simple operational amplifier is used instead of an instrumentation amplifier. Also, since the input signal size is determined solely by the choice of thermocouples, the gain for the amplifier is preset.

The 5206 LIA is fully programmable. It is also a two channel instrument so that both real and imaginary portions of the impedance can be read simultaneously. The LIA is responsible for the complete analysis of the current and voltage signals to determine the impedance. This removes the burden of analysis from the NOVA, both simplifying the required programming and more accurately dealing with extraneous noise in the signals.

The problem of extraneous noise is particularly troublesome when examining dc phenomena. It is aggravated when the samples under investigation are highly resistive (500 K $\sim$ or more) and distant from the measuring system. Therefore, precautions have been taken in building the system. All connecting cables between the various units are separated by shielded wire. Whenever possible, these same shielded cables are used in the internal circuitry of the units. As a final precaution, the power supply for the isolation amplifiers is located external to the

amplifiers themselves. These precautions result in only 10 mV of 60 Hz signal in the current signal output and less than 5 mV in the voltage signal output of the isolation amplifier.

5. Procedure

The programs developed for this system are designed for maximum versatility. The specific operational parameters of the instruments used are all selected by the experimenter. Also, the program is written so that new instruments can be easily substituted for those presently used. The operation of each instrument is controlled by independent subroutines so that an instrument change will not require a change in the main program logic.

For dc operation, the D/A unit supplies the polarizing potential for each sample. The resulting voltage across and current through a sample is read through the A/D unit. The NOVA always uses the maximum gain on the multiplexor when making a reading. The switching unit controls which cell is being monitored and whether a particular cell is being polarized or is in an open circuit configuration. For each reading taken, the NOVA also takes an estimate of the uncertainty in the reading. This uncertainty is maintained in all calculations, and reported in all final results. The exception is that when the NOVA studies the transient dc behavior, there is not sufficient time to estimate the uncertainty in any reading. This difference is handled by a special method discussed below in section 6. Fig. 6 shows a general process scheme for the dc measurements.

The NOVA will take both steady state and transient data at several user defined polarization potentials. Further, the NOVA assumes a pairing of samples so there is an internal check available. Each sample undergoes a steady state analysis at each potential in addition to two transient studies. One study is either from or to an open circuit condition to or from a set potential. The second transient study is from one potential to another, either higher or lower. The samples are paired such that each pair has one of each of the four transient studies. A transient study takes a select number of points in one second (up to 400) then one point per second for a set time period.

For the ac studies, the NOVA uses the LIA to change the signal frequency throughout the desired frequency range. The NOVA also adjusts the various LIA parameters for maximum sensitivity and minimum uncertainty. After the LIA has determined the impedance of the sample, the NOVA stores the information, and its uncertainty for later use. As with the dc, the NOVA controlled switching unit selects which sample to be analyzed.

In both ac and dc, the NOVA changes the samples' temperature by selecting the set point on the temperature controller. This is done by altering the voltage of one of the D/A channels. The NOVA determines temperature by reading the amplified signal from a thermocouple referenced to 0°C. To assure this reference is valid, the NOVA continuously monitors room temperature, referenced to the same 0°C ice bath. When the apparent room temperature changes too fast or beyond set limits, the NOVA assumes the ice bath has failed. It will not resume the experiment until the ice bath has been replaced.

Also, before accepting any data, the NOVA waits until the rate of change and fluctuation of the data decreases below limits set by the experimenter. This applies to voltage, current, and temperature from the MD unit and impedance from the LIA. Again the dc transient data is an exception to this. To decrease the fluctuation in the dc transient data, the temperature controller set point is changed to zero before the study and reset to its value immediately after the study. This eliminates the large signals induced by the furnace windings. The temperature change during this furnace shutdown during the study ($\approx 3-5$ rain) is within the uncertainty of the temperature.

6. Analysis

Due to the memory restrictions of the NOVA, the main controlling program only stores data. The specific analysis of the data is reserved for additional programs. The main program does maintain a report of all steady state and transient dc data. A comprehensive data plotting and

manipulation package is available for least squares analyses & the Ohmic and Arrhenius behavior of the samples under dc. Since analysis of ac impedance spectra is largely model dependent, the analysis is primarily experimenter dependent. The NOVA can find parameters to fit specific models, but the experimenter must supply the models.

The sole data analysis the main controlling program performs, exclusive of uncertainty, is with the transient dc data. Following the analysis of dc relaxation techniques by Joshi [3], there are several current-time or voltage-time relationships that can exist. By proper manipulation of the variable, it is possible to express each in a linear form. The authors took advantage of these linear relationships to eliminate the unnecessary transient data storage while storing the linear parameters. The NOVA performs the appropriate data transformation for each linear form and searches for any set of points that match a line. This is done by examining a set of points and determining if the correlation coefficient of the new set combined with the old set is better or worse than the old set alone. If it is better, the new points are included with the old, to start a line or continue a line. If it is worse, the computer ends the line, or makes this set the old set if no line had been started. The number of points in each set is chosen to include a full 60 Hz cycle. This tends to minimize the effects of 60 Hz noise in the transient analysis.

7. Conclusions

The calibrations performed on the A/D, D/A, and amplifier units all indicate extreme accuracy. Additionally, each was completely linear to better than the uncertainty in the measurements. This provides a high degree of confidence in the data obtained by the NOVA.

The switching unit demonstrates complete isolation of one sample from the other. The authors have not detected any effect on one sample by the presence of another. Additionally, under steady state dc conditions, the NOVA accurately determined sample resistances from 760 k Ω to 10 M Ω .

Under dc transient conditions, the NOVA is capable of consistently detecting similar linear forms across several samples. This indicates both that the 1.0mV 60 Hz noise on the current line is not a problem, and that the analysis procedure is correct.

The NOVA III computer provides a flexible heart for a coordinated measurement system. The ability to perform both dc polarization and ac impedance studies on a sample using the same equipment eliminates certain difficulties in comparing the data. The system that these authors have designed and built meets the requirements for a comprehensive measurement system for the study of mixed conductor electrolytes.

[1] A. Hooper, NATO ASI on solid state batteries. (Nijhoff, Dordrecht, 1985) p. 261.

[2] C. Wagner, in: Proc. 7th Meeting C.I.T.C.E. Lindau (1955) (Butterworths, London, 1957) p. 361.

[3] A.V. Joshi and J.B. Wagner, Jr., J. Electrochem Soc. 122 (1975) 1071.

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Figures:

Figure 1: Logic diagram of digital interfaces. Chips U1, U2, U3 and U5 are IEEE-488 transceivers. U14 and U15 are 4-b-t shift registers. For clarity, the two 4-bit BCD to binary decoders used for switch control are not shown. Signal names with a [] are connections to the NOVA bus system.

EXPERIMENTAL EQUIPMENT

Figure 2: dc polarization block diagram. For ac replace the isolation amplifier with a lock-in layer.

MAGICAL SWITCH BOX

Figure 3: Switches 1 and 2 digitally operated by control lines 1, switches 3, 4, and 5 digitally operated by control lines 2.

SWITCHING RELAY CONTROLS

a) Power Switches

b) Meter Switches

Figure 4: Control circuitry for magical switch box (a) detail of one cell of control lines 1, (b) detail of one cell of control lines 2.

AMPLIFIER DESIGN

Figure 5: General amplifier circuitry. The gain section differs for each amplifier. For voltage, the gain section is eliminated. For the thermocouple, the switches are eliminated, leaving a single set of fixed and variable resistors for a gain of 250.

Figure 6: Display status, print results, and store results when appropriate.