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TECHNICAL NOTE

Automatic scanning of log conductivity versus temperature: a time saving technique in solid electrolyte research

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1. Introduction

Much effort in materials research is presently concentrated upon the discovery of suitable solid electrolyte materials. An important parameter for these materials is the electrical a.c. conductivity as a function of temperature. This conductivity may vary over many decades, and is generally measured by means of a.c. bridge methods at a suitable audiofrequency (for instance 1 kHz). Generally, such measurements are rather time-consuming. Scanning methods for solid electrolytes that have been proposed and used include measurement of transition entropies [1] and NMR techniques [2, 3].

However, a direct measurement of the (audio-frequency) a.c. conductivity as a function of temperature gives much more easily interpretable results. In this paper we will describe the build-up and use of a device which was developed for continuous and unattended scanning of the a.c. conductivity as a function of temperature. The resistance range that can be covered is from 10 Ω to 1 MΩ. The temperature range is from ambient to 1000°C. (These limitations can, however, easily be shifted.)

The logarithm of the specific a.c. conductivity at 1 kHz is plotted automatically versus temperature on an X, Y–recorder. The method will be referred to as automatic temperature versus log conductivity or ATLC-scanning.

2. Log conductivity device

The basic idea was to place the sample in a potentiostatic circuit. The voltage difference over the sample is controlled sinusoidally by use of a Wien bridge attached to one input of the potentiostatically used operational amplifier. The current through the sample is amplified and after rectification fed to a logarithmic amplifier. The signal from this amplifier may be fed to one input of an X, Y–recorder. A temperature signal from a thermocouple may be fed to the other input of the X, Y–recorder. The circuitry for the log (a.c.) conductivity device is given in some detail in Fig.1.

One of the problems to be overcome is that when using a fixed a.c. voltage level over the sample (we used 1·00 V effective), the signal-to-noise ratio becomes very unfavourable at high resistance values of the sample (implying low currents). On the other hand one may not use too high an a.c. voltage level, as one should avoid Joule heating at low resistance values of the sample. Thus, it was impossible to use one fixed current measurement resistor in the potentiostatic circuit. In this device we have thus chosen for current amplification per decade. With the use of comparators at the output of the rectifier circuit it was possible to select the current amplifiers for the appropriate decade ranges. (This gave a much more favourable signal-to-noise ratio.) A further problem was posed by the fact that the rectifier circuit only 'works' above a certain voltage level (0·7 V) with the penalty of a nonlinear dependence of the rectified signal with respect to the effective overall current through the sample. This was solved by switching per decade of 'measured' resistance and by current amplification per decade. An appropriate voltage signal is thus fed to the rectifier circuit for each individual decade. The result of this is that for each decade, the same voltage range is covered at the output of the logarithmic amplifier. The switch

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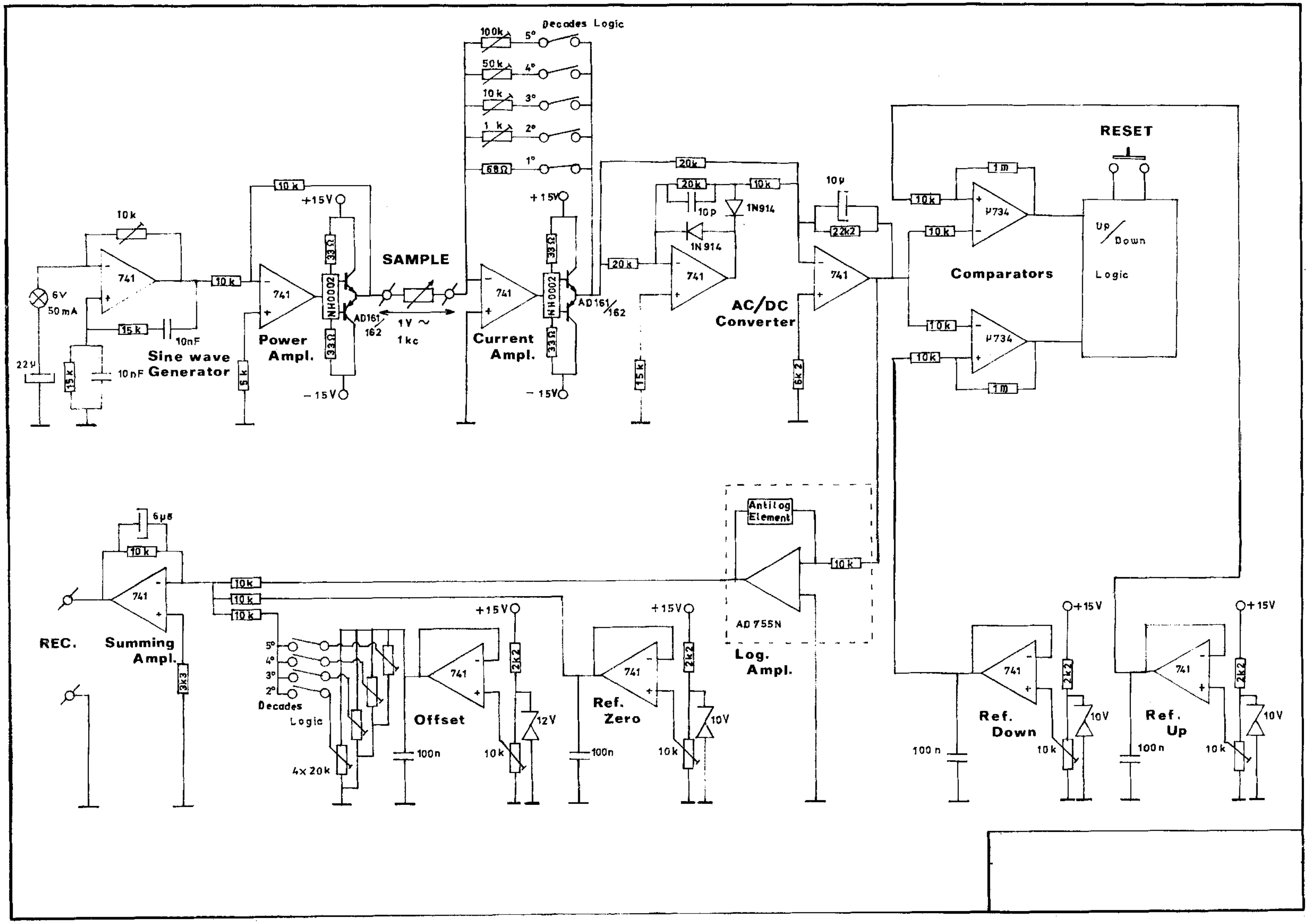

Fig. 1. Circuitry scheme of the log conductivity device.

points for stepping to a higher or lower decade are somewhat shifted with respect to each other, such as to make a trivial choice of the decade range possible. After logarithmic amplification per decade, an appropriate offset level was added to the logarithmic signal, such as to smoothly connect the decades. In this way, over five decades of resistance are covered, (roughly) from 10 Ω to 1 MΩ. The overall accuracy is better than 5% of the real conductivity.

3. Sample mounting and thermal scanning

Samples to be subjected to ATLC scanning were prepared in the form of pressed pellets of the powdered material, with pressed-on silver discs. The sample was placed in a quartz cell with platinum leads in a quartz tube oven. The oven was supplied with an Eurotherm thyristor regulator, adapted for temperature programming by use of an external potentiometer driven by an electromotor with tunable rotation rate. This enabled a controlled heating and cooling rate of the oven of 1°C min^{-1} or less, down to 0·03°C min^{-1}. (Higher rates than 1°C min^{-1} may be applied, but this is not advisable because of undesirable lagging effects.) In practice, we always start at the highest possible temperature under the melting point of the sample and record a cooling curve first. If this is not done, then the electrode may not be in good equilibrium with the electrolyte, leading to irreproducible and erroneous results. (Sintering of the electrolyte may also play a role.)

Fig. 2 shows a typical ATLC scan on a —Na_2SeO_4—doped—Na_2WO_4 pressed pellet. By appropriate zero-point adjusting of the logarithmic scale, depending upon the geometrical factor of the sample, the specific conductivity is given directly on the logarithmic scale. By comparison of heating and cooling ATLC scans one may get information about hysteresis effects, about metastable phase occurrence and so on. As compared with the more conventional 'point by point' a.c. bridge method for a large number of temperature steps, and subsequent plotting, we have here the advantages of unattended operation (including overnight periods) and more complete information from continuous recordings. For scanning purposes, these advantages mostly outweigh the greater precision of bridge readings.

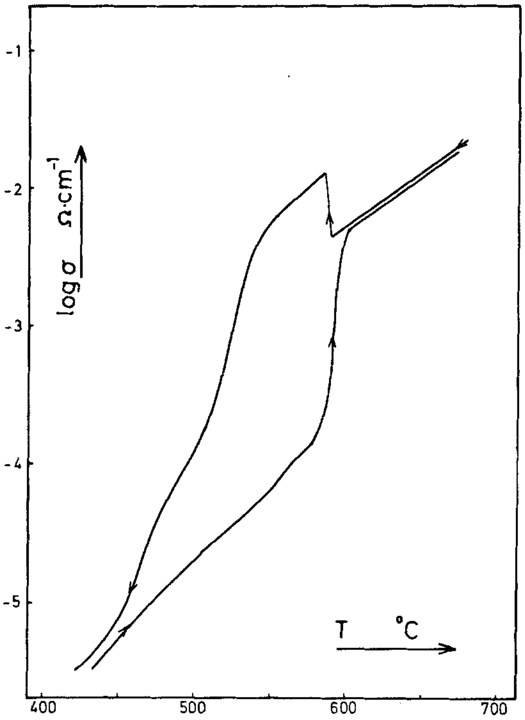

Fig. 2. Typical ATLC cooling (upper) and heating (lower) scans on solid Na_2WO_4, doped with 0·6 mol % Na_2SeO_4. Cooling and heating rates are both 1°C min^{-1}. The discrepancy between heating and cooling runs is due to hysteresis effects and metastable phase extension, caused by the dopant. The 'jumps' in the conductivity at 590°C point to relatively fast phase transitions.

4. Applications of ATLC-scanning

The method was developed to enable fast scanning of the electrical conductivity of possibly interesting solid electrolytes. Apart from this it may be used as an additional technique in the investigation of certain phase diagrams. Furthermore, it might have applications in the kinetic investigation of phase transformations, as the overall conductivity is a measure of the amount of both phases present at a non-equilibrium situation during the phase transition.

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