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SHORT COMMUNICATION

Impedance measurement on Pb/H_2SO_4 batteries

M. KEDDAM, Z. STOYNOV,* H. TAKENOUTI

Groupe de Recherche no. 4 du C.N.R.S. 'Physique des Liquides et Electrochimie',
associé à l'Université P. et M. Curie, 4 place Jussieu, 75230 Paris Cedex 05, France

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1. Introduction

Relatively few works have been carried out on Pb/H_2SO_4 batteries from an electrochemical kinetics point of view. This is partly due to the complexity of the chemical and electrochemical reactions occurring on plates but mainly because the system is not a constant one. The current continuously modifies the electrode structures and their properties [1–3], so that, strictly speaking, no steady-state can be defined in this system. Thus, it is scarcely possible to use the classical methods of electrochemical kinetic investigations such as the analysis of polarization curves.

The use of transient methods seems to be more adequate to investigate the electrode processes of such systems. If the system is disturbed by a very small measuring signal so that its response remains linear, its impedance can be defined. This allows the analysis of the dynamic behaviour of the system [4]. If the direct polarizing current (bias current) I is equal to zero and also if the auto-discharge of the battery is negligible, the structure and properties of both plates may be regarded as constant. In this particular case, the steady-state can be defined. On the contrary, during the charge or discharge processes of a battery, if the measuring period is short enough, the evolution of the electrode structure and other properties affecting cell impedance may be kept to the same order of magnitude or smaller than the errors of measurement. In this case, the system under investigation is considered to be in quasi-steady-state. Of course, the lowest frequency at which the impedance can be properly explored depends on the measuring error and also on the rate at which the system changes.

The purpose of this note is to demonstrate that it is technically possible to measure the impedances of electrochemical generators by means of a transfer function analyser over a very wide frequency range. The impedance measurements are performed between two terminals of a battery, corresponding to the overall dynamic behaviour of the cell, as well as separately on positive and negative plates. Some preliminary results obtained on a commercially available Pb/H_2SO_4 battery during a charge and discharge cycle are given.

2. Experimental

2.1. *Experimental conditions*

The Pb/H_2SO_4 battery used in this work is a commercially available (DININ 3M7) low capacity model (6 V–7 A h). The impedance measurements were performed at room temperature after several charge–discharge cycles. The charge current is 0·35 A whereas that of discharge is − 0·7 A. For the study of the fully charged battery, after passing the charging current for 24 h, the battery was kept at rest potential without any current for 3 h before starting the impedance measurements. We have also noticed that, as well as the cell voltage, the cell impedance changed, after current interruption, and the steady-state can only be attained after this waiting period.

For the study of the completely discharged battery, the discharge current was imposed until the output voltage became 5·5 V. After that, the battery was left on open circuit for 4 h before the impedance measurements were commenced. In these two cases, as there is no d.c. current, the steady-state can be obtained.

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* On leave from: Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1000, Bulgaria.

2.2. *Measuring device*

Electrochemical generators have, in general, very low internal impedances. Thus, it is more easy to regulate current than voltage. The experimental set-up of the impedance measurements including current regulation is shown in Fig. 1. It can be divided into three main functions: regulation; measurement; and recording.

The current passing through the battery is controlled [5] by the voltage drop across a standard resistance R_{st} having a very low self-inductance (1 Ω, type RCL 7040HS). The adder circuit Σ enables the measuring signal ΔI, issued from the generator output of a transfer function analyser (TFA), to be superimposed on a bias current I.

The impedance measurements are performed by means of a digital transfer function analyser (SCHLUMBERGER, SOLARTRON 1172) which compares, by a correlation procedure, the two input signals X and Y with respect to the output signal ΔI [6]. The TFA used operates in the frequency range of 10^4 to 10^{-4} Hz. The X signal is the amplified a.c. voltage between the two terminals of the battery in the case of the overall impedance when one of the plate impedances is measured. A reference electrode, saturated mercurous sulphate, is inserted from the aperture of the element nearest to the standard resistor R_{st}. The voltage response is in this case picked up between the reference electrode and the terminal connected to R_{st}. Y is the current signal ΔI amplified by means of DI. The TFA gives directly complex values of Y/X i.e. the real part R and the imaginary part G. Therefore, the impedance Z of the system under investigation is given by $Z = R + jG$ (where $j = \sqrt{-1}$) with a proportionality coefficient depending on the gains of the two amplifiers DV, DI and on the value of R_{st}.

Particular care has been taken with the current and voltage measurements so that the resistances of the wires affect the measurement accuracy as little as possible. The automatic frequency sweep

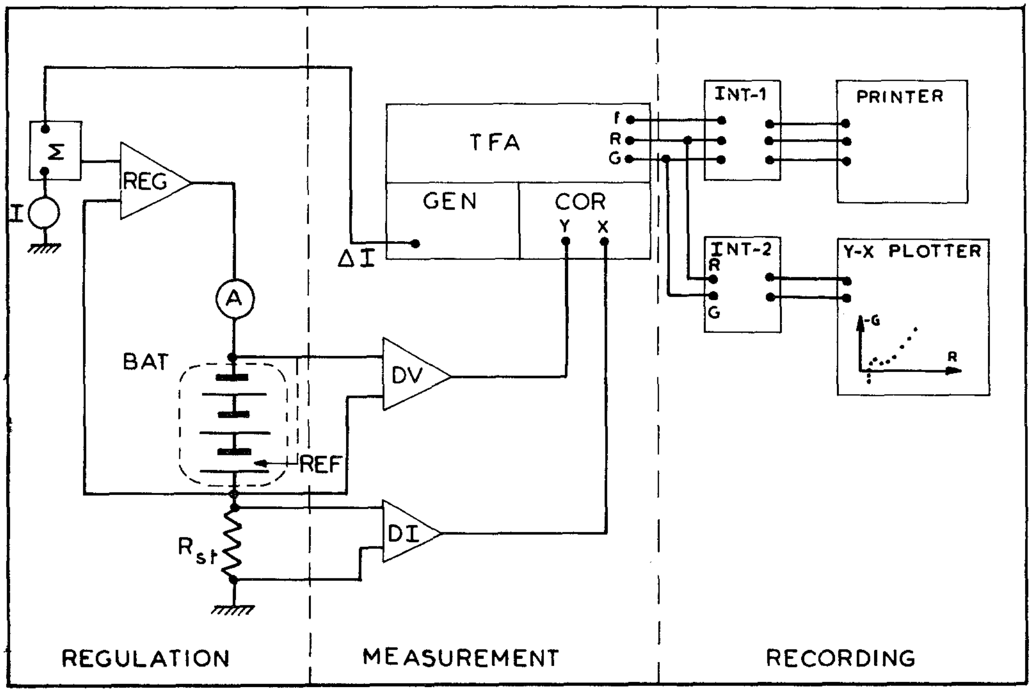

Fig. 1. Experimental set-up for impedance measurement: this figure corresponds to the measurement of the overall impedance. A reference electrode is used as indicated by the dotted line in order to measure one of the plate impedances for voltage pick-up. Σ: adder; I: signal for the bias current; ΔI: signal for the measuring a.c. current; REG: current regulation device; A: ammeter; BAT: Pb/H_2SO_4 battery; REF: reference electrode SSE; R_{st}: standard resistance; TFA: transfer function analyser; GEN: sine wave generator; COR: correlator; DV: differential amplifier of a.c. voltage signal; DI: differential amplifier of a.c. current signal; INT-1, INT-2: interfaces.

and also the automatic choice of input voltage range allow, in connection with the automatic data recording, fast measurements of cell impedance.

The recording includes two different functions, namely digital recording (DATA DYNAMIC 390) and the plotting of the impedance diagram on an X–Y recorder (SEFRAM TGM 164). The interface INT-1 (SOLARTRON DATA TRANSFER UNIT) checks the printing whereas the interface INT-2 (SOLARTRON 1180 PLOTTER INTERFACE) converts the digital data into analogue form and operates the X–Y pen recorder.

Using this experimental set-up, measurements of impedance of a few mΩ can be performed over the whole frequency range mentioned above.

3. Results

The impedance diagrams obtained between two terminals for a fully charged ($I = 0$), a discharging ($I = -0{\cdot}5$ A) and a completely discharged ($I = 0$) Pb/H_2SO_4 battery are given in Figs. 2–4 respectively. The d.c. voltage on open circuit of a charged battery between the two terminals was 6·45 V.

After having carried out the impedance measurements on the charged battery, a discharging current equal to − 0·7 A was imposed. When the voltage between the two terminals under this discharging current reached 6·05 V, the current was lowered to − 0·5 A. The impedance measurements were started when the voltage stopped changing (after about 10 min.). The frequency range explored was limited to $f \geqslant 0{\cdot}01$ Hz so that the system remained virtually unchanged during the measurements. (In this case they take about 20 min). The voltage between the two terminals at $I = -0{\cdot}5$ A changed from 6·058 to 6·053 V. Furthermore, at measuring frequencies lower than this value, the change of bias potential V cannot be neglected with respect to ΔV even though the principle of impedance measurement by correlation calculation corresponds to the use of a very narrow band width filter. $\Delta I = 50$ mA peak-to-peak was found to be the maximum magnitude which can be used for impedance measurements in the low frequency range. At higher amplitudes for ΔI, the response is no longer linear. The corresponding ΔV at $f = 0{\cdot}01$ Hz is thus about 5 mV peak-to-peak.

After these measurements, the discharging current of − 0·7 A is again imposed until the voltage between the two terminals becomes 5·5 V. Then the current I is reduced to zero. The impedance measured at 1 Hz as well as the terminal voltage indicate that 4 h needs to elapse before the system is in a steady-state condition.

On these three figures (2–4), it is observed that the imaginary component of the cell impedance is cancelled out at a frequency close to 1 kHz. At

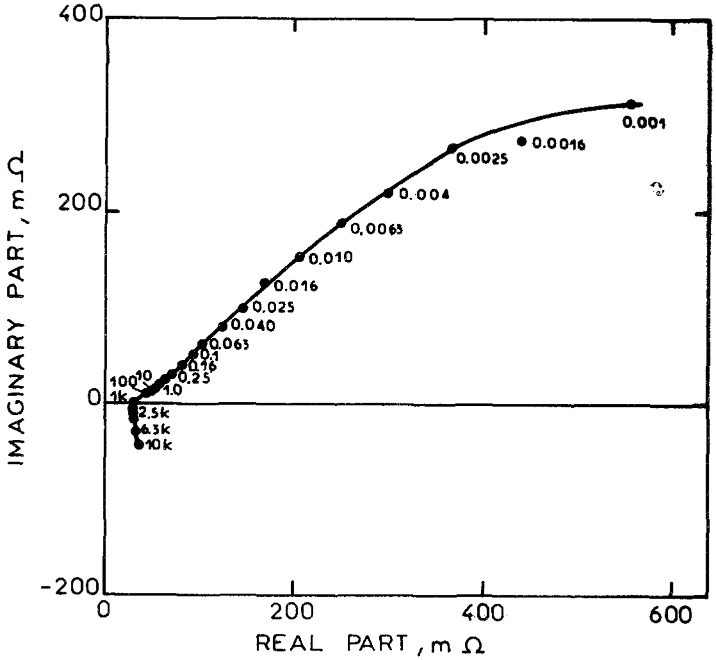

Fig. 2. The impedance diagram of the fully charged battery (6 V–7 A h) measured between two terminals, bias current $I = 0$.

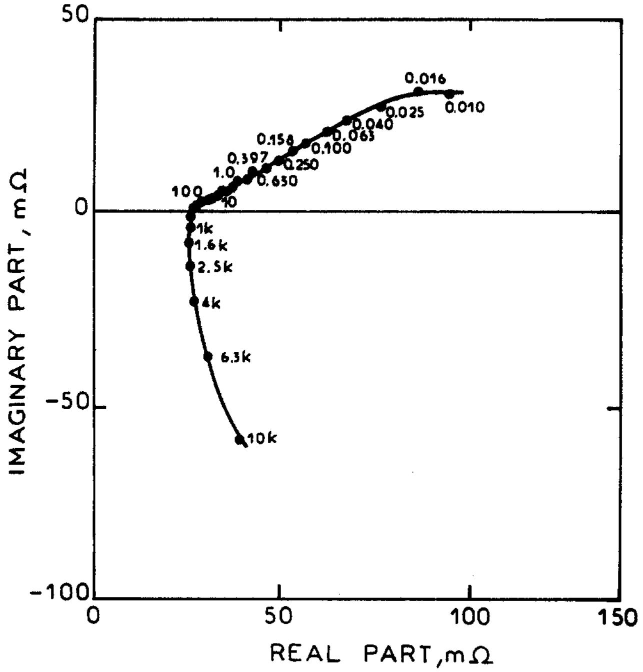

Fig. 3. The impedance diagram during discharge measured between two terminals. Battery see Fig. 2. Discharging current $I = -0{\cdot}5$ A.

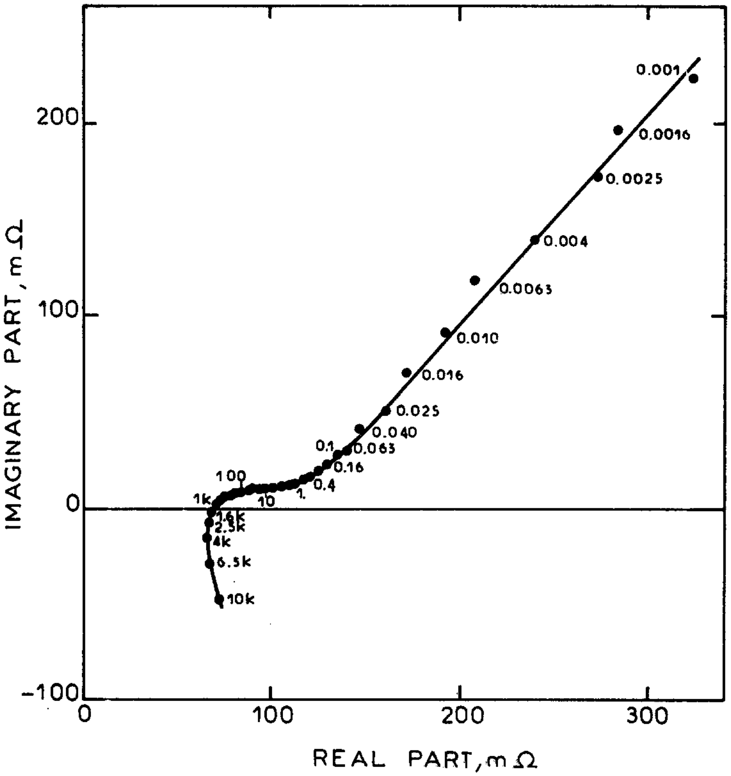

Fig. 4. The impedance diagram of a completely discharged battery measured between two terminals. Bias current $I = 0$.

higher frequencies, the impedance is inductive whereas at lower frequencies it is capacitive.

The self-inductive nature of electrochemical power sources at high frequencies has already been observed by many authors [7–9]. These figures show that the value of the self-inductance is almost independent of the charging state of the battery as well as of the bias current. It is equal to about 1 μH. This self-inductance may not thus be of a faradaic nature but may rather be related to the geometrical nature of conductors and electrodes. Phenomena which depend on the charging state or on the current are to be seen through their effects on the capacitative behaviour, especially in the very low frequency range ($f \leqslant 1$ Hz). It is also to be noted that the self-inductance observed at high frequencies is schematically shunted by a parallel resistance of about 0·6 Ω.

A correction was made for the influence of the self-inductive term on the capacitative impedance, which contains interesting information. It is found that the limit at high frequencies of the capacitative arc increases continuously from 25 to 60 mΩ during the discharge of the battery. This resistance may be considered, by analogy with the usual electrode impedance, as the electrolyte resistance including that of the plates and the connectors. However, the change of this resistance value is too large to be solely attributed to the change of electrolyte conductivity due to the acid dilution by discharge. The change of the surface structure, particularly that of the surface coverage by non-conducting reaction products on the negative electrode during the discharge may partly explain the difference between the increase of apparent electrolyte resistance and that of electrolyte resistivity.

However, the measured impedance between two terminals concerns both positive and negative

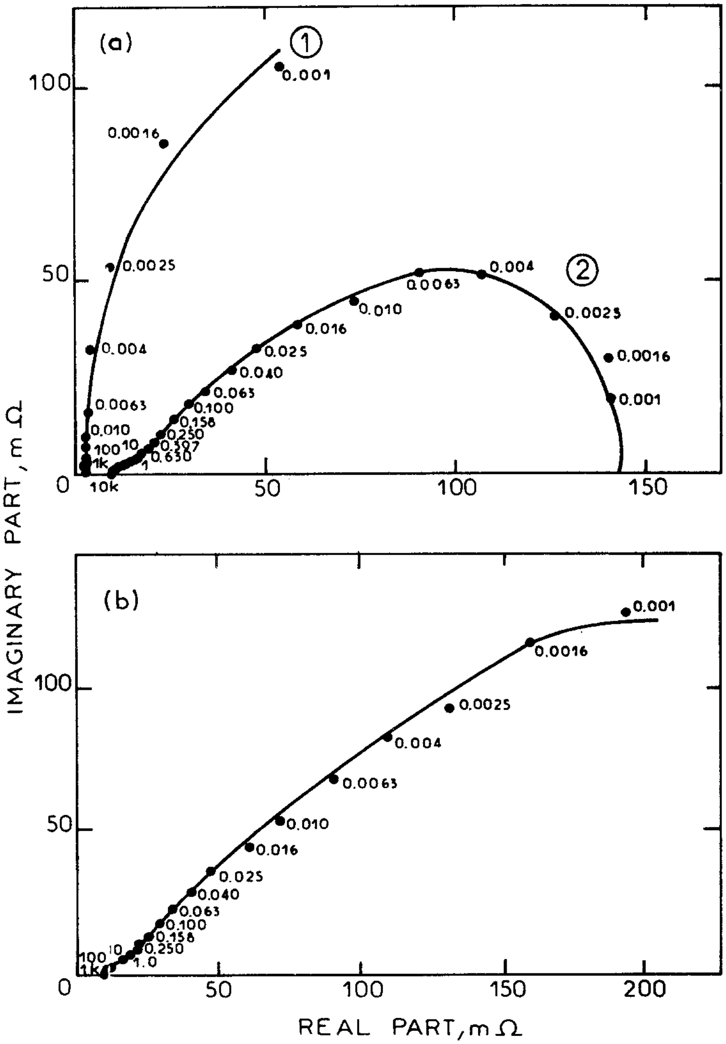

Fig. 5. The impedance diagrams of the fully charged battery. The self inductance at high frequencies is eliminated. Bias current $I = 0$. (a) Curve 1: positive plate; curve 2: negative plate. (b) The sum of $a - 1$ and $a - 2$ giving the overall impedance (c.f. Fig. 2). The impedance at a given frequency is one-third of that observed in Fig. 2, since the battery consists of three series elements.

plates. By using a reference electrode (mercurous sulphate in saturated K_2SO_4 : SSE) introduced into the cell through the filling aperture, the impedance of each plate can be measured separately. The impedances of the positive plate (curve 1) and the negative plate (curve 2), measured independently on the fully charged battery and at the bias current zero, are shown in Fig. 5(a). These curves are obtained after eliminating the effect of the high frequency self-inductance. From curve 1, it can be seen that the impedance of the positive plate remains practically as a pure resistance at frequencies higher than 1 Hz. For lower frequencies, a large capacitative arc corresponding to a very low time constant is observed. Curve 2 shows that the impedance of the negative plate is analogous to that of a fast Redox system. It behaves like the impedance arising from a Nernst's diffusion layer of finite thickness at frequencies lower than 1 Hz. At higher frequencies, a small capacitative arc can be distinguished.

It is verified that the sum of the impedances of the positive and the negative plates gives an overall impedance [Fig. 5(b)] which is equal to that measured between two terminals (c.f. Fig. 2) by taking into account the number of elements in series (= 3). It is very important to note that the impedances of both the positive and the negative plates change in the same frequency range ($f \leqslant 1$ Hz) so that the separation of their relative contributions is only possible by impedance measurements on each plate.

Lastly, we have verified that this experimental set-up can be used without any modification for impedance measurements of primary batteries such as the Leclanché cell.

4. Conclusions

The impedances of a commercial Pb/H_2SO_4 battery have been measured under different charging conditions. It was found that the impedance variations spread over a very wide frequency range. Nevertheless, the marked change of impedance with respect to the variation of the states of the plates appeared particularly in the low frequency range ($f \leqslant 1$ Hz).

The time constants of the processes occurring at the positive plate and at the negative one are not very different. Thus impedance measurements must be made on each plate in order to investigate the kinetics of the electrochemical phenomena. Even without interpretation, the results of these impedance measurements can be used to characterize the quality and the states of batteries in a sensitive way.

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