

IMPEDANCE OF POROUS ELECTROCHEMICAL SYSTEMS: STUDY OF THE NEGATIVE ACTIVE MASS OF THE LEAD/ACID BATTERY

K. V. RYBALKA* and L. A. BEKETAEVA

A.N. Frumkin Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow (U.S.S.R.)

Introduction

In principle, valuable information about the physicochemical behaviour of porous electrochemical systems can be obtained from impedance measurements. The latter assist in understanding the porous structure of the electrode (and changes to it during operation), the reagent distribution inside the electrode, and the mechanism of the electrochemical processes.

Experimental

The applicability of the impedance method to lead/acid battery electrodes is illustrated here through studies of the active mass of the negative electrode. The active mass was prepared according to methods used in battery plants. It is well known that impedance values of a lead/acid battery are distorted at frequencies above 100 Hz by the inductance of the connecting wires and the current collectors. This is due to the very low values of the battery impedance. In order to eliminate these complications, special electrodes were employed in the impedance investigations. These electrodes contained a very small amount of active mass. With this approach, it was possible to measure the impedance up to a frequency of 50 kHz.

Results

Figure 1 shows the impedance plot for the charged negative active-mass under low cathodic polarization. The character of this plot is typical for pores of cylindrical shape [1]. Therefore, it is possible to describe the pores by two parameters, namely, a radius, r , and a length, l .

A study has shown that the phase shift for the active mass is almost half that for a smooth electrode; this is in agreement with the impedance

*Author to whom correspondence should be addressed.

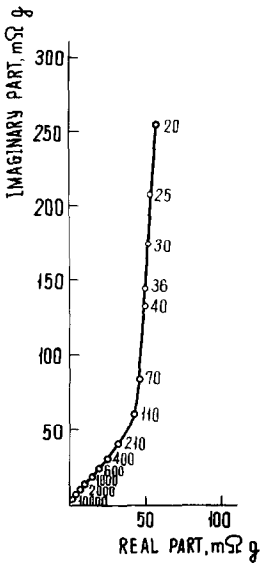


Fig. 1. Impedance diagram for charged negative active mass. Numbers denote frequency in Hz.

theory for porous electrochemical systems [2]. At a frequency of 20 Hz, the phase shifts for both electrodes are practically equal. Therefore, the charged, pasted, negative electrode of a lead/acid battery at frequencies of 20 Hz, and lower, behaves not as a porous system but as a smooth electrode with a highly developed surface area. Hence, in this frequency region, impedance measurements can be used to evaluate the true surface area of the active mass. For higher frequencies, the impedance method will give erroneous values of the specific surface area.

It is known [1] that the parameters of the porous structure can be easily calculated for ideally polarizable electrodes in absence of electrochemical processes. The requirements of ideal polarizability are unrealizable in most industrially important electrochemical systems. Therefore, in order to use impedance measurements to determine the porous electrode structure accurately, a method of analysis of impedance data, taking into account the electrochemical reaction, has been developed. The treatment is based on the general equation [2] describing the pore impedance:

$$Z_p = (RZ)^{1/2} \coth(R/Z)^{1/2} l \quad (1)$$

where R and Z are the electrolyte resistance and the surface impedance (referred to unit pore length), respectively.

Discussion

Analysis of experimental data based on eqn. (1) is very complicated, but in the region of low frequencies, the most informative for the analysis

of the porous systems, the equation for the impedance of a porous electrode, Z_e , can be simplified to:

$$Z_e = l^2/3kV_p + \text{Re}(Z_s)/S + j \text{Im}(Z_s)/S \quad (2)$$

where: Z_s is the surface impedance per unit surface area; k is the conductivity of the electrolyte; V_p and S are the specific pore volume and electrode surface area, respectively. In a number of cases, when the surface impedance Z_s is known, eqn. (2) allows easy calculation of the parameters of a porous electrode structure in the presence of electrochemical processes.

For different states of charge of the negative active mass, the impedance plot over a wide range of frequencies is close to a semi-circle. In this case, the surface impedance, Z_s , can be represented by a parallel connection of the electrical double layer capacitance, C_d , and a reaction resistance, R_F . As a consequence, eqn. (2) can be modified in order to determine the porous structure parameters even when the surface impedance is unknown:

$$\text{Re}(Z_e) = l^2/3kV_p + (1/C_d R_F) \cdot \text{Im}(Z_e)/\omega \quad (3)$$

It follows, from Fig. 2, that eqn. (3) describes satisfactorily the experimental data for the active mass of the negative electrode. It must be emphasized that the value of $l^2/3kV_p$ for electrodes under cathodic polarization and in equilibrium conditions is the same.

The shape of impedance diagrams for many technically important electrochemical systems is very close to a semi-circle. Therefore, it is expected that eqn. (3) may be useful for the treatment of a large range of porous electrochemical systems.

The charge or discharge of an active mass results in a change in the volumes of the solid and liquid phases. This allows determination of the pore

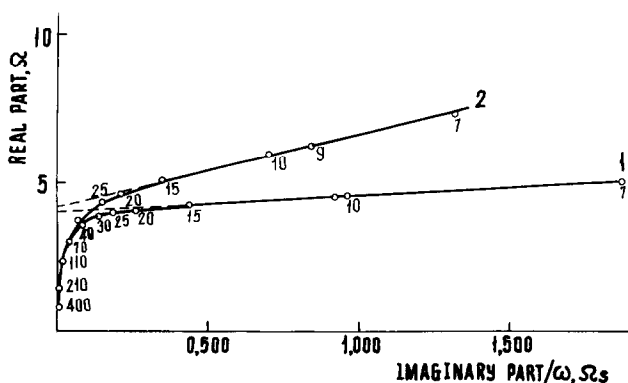


Fig. 2. Plot of real component of impedance against imaginary component divided by angular frequency: 1, cathodic polarization; 2, equilibrium conditions.

length, l , and pore volume, V_p , directly from impedance data [3]:

$$1/R_0 = \frac{3k V_p^0}{l^2} + \frac{3k \Delta V}{2Fl^2} q \quad (4)$$

where: R_0 is the intercept of the straight line according to eqn. (3) and the ordinate; V_p^0 is the pore volume in the discharged active mass; ΔV is the mole volume change during charge; q is the quantity of electricity. Thus, impedance measurements of a porous electrode during the charge or discharge process enable the porosity and the pore length to be determined as a function of the state-of-charge. Combined with the values of surface impedance or double-layer capacitance, these measurements also provide values for the average pore radius and the specific surface area of the active mass.

From the theory of porous electrochemical systems, it is known that the depth of penetration of an electrical signal into the electrode increases with decreasing frequency. Therefore, there is the possibility of conducting a depth analysis of the electrode. Taking into account the average value of the pore radius in the active mass of the negative electrode ($\sim 4 \times 10^{-4}$ cm) and the differential double-layer capacitance of lead in presence of an expander ($\sim 10 \mu\text{F cm}^{-2}$), a calculation was made of the depth of penetration of the electrical signal into the active mass in 5 M sulphuric acid solution. For frequencies of 20, 70, and 210 Hz the penetration is equal to 0.25, 0.13 and 0.08 cm, respectively.

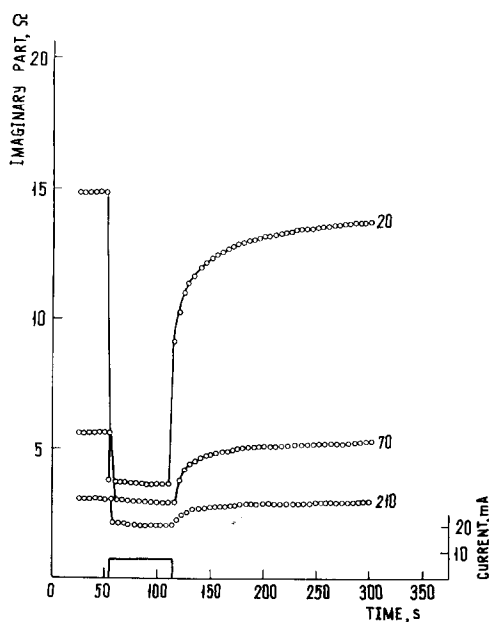


Fig. 3. Plot of imaginary component of impedance and of anodic current as a function of time. Numbers denote frequency in Hz.

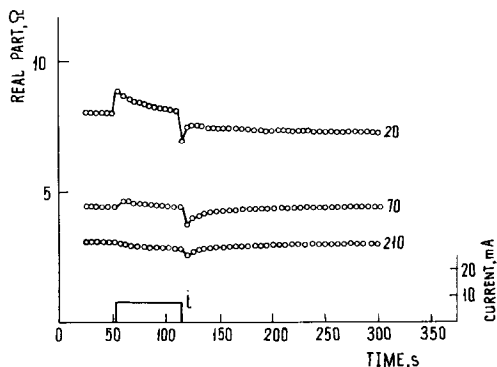


Fig. 4. Plot of real component of impedance and of anodic current as a function of time. Numbers denote frequency in Hz.

Figures 3 and 4 illustrate the dependence of both impedance components of a pasted electrode on time for different frequencies. The slow increase of imaginary component with time just after the anodic current is switched off is obviously due to the slowness of the lead sulphate crystallization and/or to the recrystallization of freshly formed lead sulphate. It is clear from Fig. 3 that these processes determining the return of the system to the equilibrium state in the bulk of the active mass and on its surface are the same.

The value of the real component of the impedance of the active mass is dependent on the ratio of the electrolyte resistance in the pores and on the surface impedance. Figure 4 shows that for a frequency of 20 Hz, at which all the parts of the porous electrode are accessible to measurement, the anodic polarization results in an increase in the real component of the impedance. This is caused by a decrease in the sulphuric acid concentration inside the electrode. By contrast, for a frequency of 210 Hz, when only the external part of the electrode takes part in the measurements, the anodic polarization results in a decrease in the real component of the impedance. The latter is due to less depletion of sulphuric acid in the surface layer of the active mass compared with that in the bulk.

Conclusions

The above results show that the impedance method enables porous electrodes to be subjected to a depth analysis so that, at least qualitatively, an evaluation can be made of the electrochemical behaviour of different parts of these electrodes.

References

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