

Impedance measurements on porous zinc electrodes operating under starved electrolyte conditions

J. Jindra*

J. Heyrovský Institute of Physical Chemistry and Electrochemistry, 182 23 Prague 8 (Czech Republic)

D. Becker-Roes

Institute of Chemical Technology, 6100 Darmstadt (Germany)

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Abstract

The electrochemical impedance of the zinc electrode was measured in starved electrolyte conditions. Measurements were made on electrodes in different states-of-charge. The results were analysed by using an equivalent circuit. The measured impedance spectra are similar to those measured on a flooded system.

Introduction

Interest in classical nickel–zinc batteries has increased considerably in recent years [1–4]. This is because of zinc is, in contrast to the hitherto used cadmium, relatively cheap and harmless from the ecological point of view. Moreover, its electrode potential and capacity in Ah/kg are higher. On the other hand, there are some disadvantages, such as the solubility of the oxidation product in the electrolyte, formation of zinc dendrites, and evolution of hydrogen [2].

According to recent papers [5–9], the plastic-bonded zinc electrodes are usually negative. The sintered-type nickel electrodes are usually positive. The sintered-type nickel oxide electrodes serve as positives.

With sealed secondary nickel–zinc batteries, it is important to remove the oxygen formed during charging at the nickel oxide electrode. This is achieved by the so-called oxygen cycle: the oxygen evolved is subsequently reduced at the negative electrode, while the internal pressure reaches a steady value as a result of the balance between the oxygen evolved and oxygen reduced. This process can only be realized if the volume of the cell electrolyte is restricted, so that the cell operates under ‘starved electrolyte’ conditions.

The faradaic impedance of plastic-bonded zinc electrodes operating in an excess of the electrolyte was measured by Hampson and McNeil [10], but no data are available on zinc electrodes operating in a reduced volume of electrolyte. The purpose of this work was to examine the latter.

*Author to whom correspondence should be addressed.

Experimental

Plastic-bonded zinc electrodes of dimensions 5 cm×4 cm were prepared by pressing a dry mixture of 93 wt.% ZnO, 5 wt.% polytetrafluoroethylene (PTFE) and 2 wt.% PbO onto a lead-plated brass net. A small porous polypropylene bag (Celgard 3401, Celanese, USA) was used as a separator. A sintered nickel oxide electrode of the same size served as a counter electrode, which was separated with a polyamide fabric (Viledon, K. Freudenberg, Germany). The electrode pack was encompassed with a corrugated, perforated polyvinylchloride (PVC) sheet and placed in a prismatic nickel-plated steel vessel together with a small Hg/HgO reference electrode. The cell casing was closed with a Plexiglass lid through which electric leads passed. A minimum volume of a 7 M KOH solution was added only just to make possible the functioning of the zinc electrode and the oxygen cycle. Thus, the cells operated with the matrix electrolyte.

The impedance was measured potentiostatically with an Impedance Measurement System IM5d, Zahner, Germany, in the three-electrode mode in the frequency range from 10 kHz to 10 mHz, on both 'charged' and discharged electrodes. In reality, the 'charged' electrodes were not fully charged since their charging was stopped at the moment when the positive electrode began to evolve oxygen, which was reduced at the negative one.

The impedance was measured always after attaining a steady electrode potential value (against the Hg/HgO reference). The cells were charged and discharged galvanostatically at a current of 100 mA. All potential values are given against Hg/HgO electrode.

Results and discussion

The Nyquist diagram for a 'charged' zinc electrode with a rest potential of -1325 mV (after 24 h idling) is shown in Fig. 1. It consists of three parts:

(i) a small semicircle with a diameter of approximately 12 m Ω in the high-frequency region, indicating a low charge-transfer resistance of the electrode, i.e., a large internal surface area;

(ii) a nearly-horizontal transition region corresponding probably to the adsorption of OH⁻ ions on zinc, and

(iii) a low-frequency portion typical for a diffusion process.

Figure 2 shows the Nyquist diagram of a discharged zinc electrode after 24 h idling, measured at the stationary (rest) potential of -1283 mV. The semicircle is practically the same as in Fig. 1, but the horizontal transition region is higher and the diffusion part is located beyond the measuring range. The series resistance is the same (94 m Ω) as with the charged electrode, as given by the high-frequency limit. This corresponds mainly to the electrolyte resistance.

Figure 3 shows the dependences of impedances and phases of 'charged' and discharges zinc electrodes on frequency. The course of curves is not surprising.

The impedance spectra measured on flooded system [10] and those measured under starved electrolyte conditions are similar for the case of the high state-of-charge of zinc electrode. Also, some impedance parameters, e.g., the electrolyte resistances, are nearly like: 70 m Ω /cm² [10] and 94 m Ω /cm² (Fig. 1). It seems that the restricted amount of the electrolyte in a hermetic cell affects little the impedance characteristics of the charged zinc electrode. At the discharged electrode, the similarity of impedance

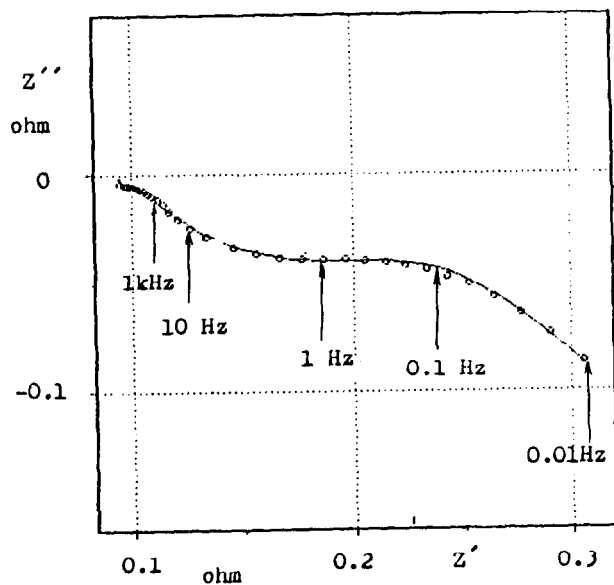


Fig. 1. Nyquist diagram (impedance) for the 'charged' zinc electrode; the curve: measured values, and points: calculated values.

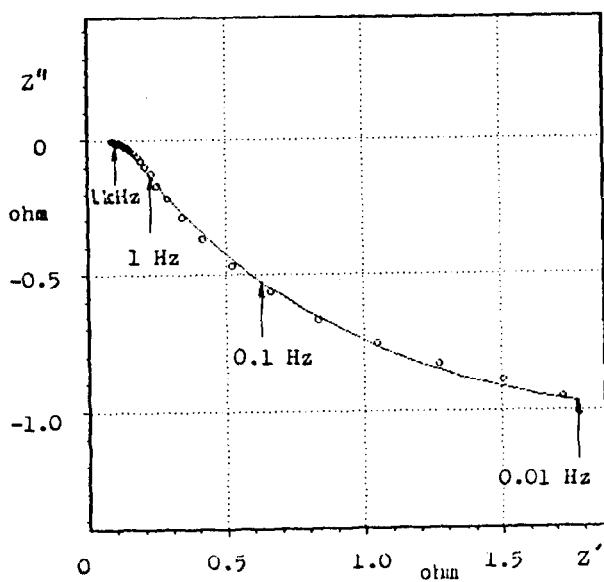


Fig. 2. Nyquist diagram (impedance) for the discharged zinc electrode; the curve: measured values, and points: calculated values.

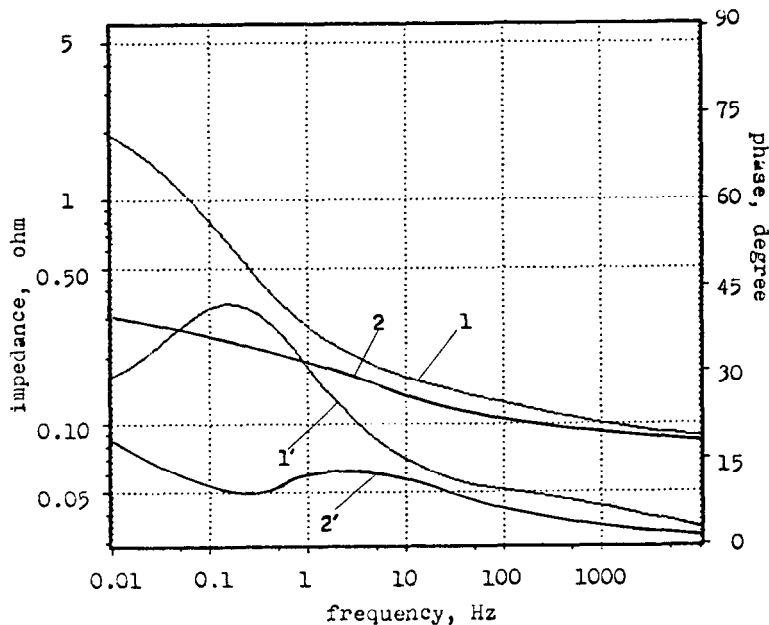


Fig. 3. Bode diagram for discharged and 'charged' zinc electrode: (1) impedance, discharged zinc; (1') phase, discharged zinc; (2) impedance, 'charged' zinc, and (2') phase, 'charged' zinc.

characteristics is not expected due to a greater chance of eqn. (2) in flooded systems. The following reactions can be expected to proceed at the zinc electrode:

(i) discharging:



(ii) dissolution of $\text{Zn}(\text{OH})_2$:



(iii) formation of a ZnO layer:



This layer grows further as further Zn^{2+} ions diffuse through it and react with zincate ions at the $\text{ZnO}/\text{Zn}(\text{OH})_2$ interface, where also the following parallel reaction may proceed:



To model the impedance characteristics of the studied electrodes, we consider the equivalent circuit shown in Fig. 4. It incorporates the electrolyte resistance, R_6 , the charge-transfer resistance, R_4 , the resistance of the ZnO layer, R_2 , the Warburg diffusion impedance, W , the capacity of the double layer on Zn , C_3 , and the capacity of the double layer on ZnO , C_5 .

The impedance of the capacitor, C_3 , cannot be expressed by the simple classical formula as $1/(i\omega C_3)$ corresponding to a phase angle $\phi = -\pi/2$. Most electrochemical processes show a different behaviour: the absolute value of the phase angle is generally smaller than $\pi/2$, i.e. $|\phi| = \alpha\pi/2$, where $0 < \alpha < 1$. Therefore, we set:

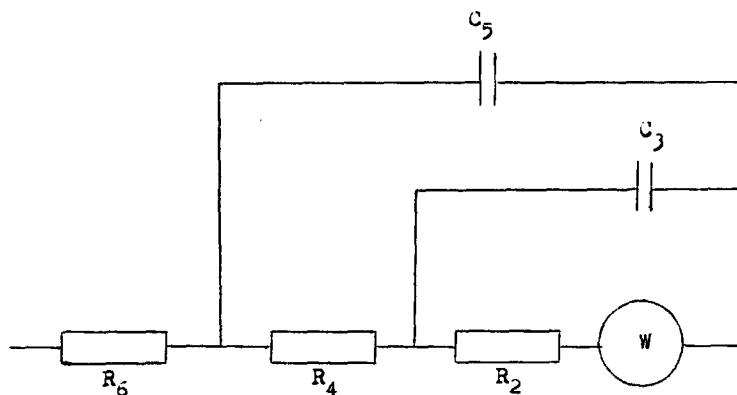


Fig. 4. Proposed Randles equivalent circuit used to model the impedance spectra of the zinc electrode.

TABLE 1

Values of circuit elements obtained by modelling the impedance spectra of 'charged' and discharged zinc electrodes under starved electrolyte conditions

E (mV) vs. Hg/HgO	W ($\Omega \text{ s}^{-0.5}$)	R_2 ($\Omega \text{ cm}^{-2}$)	R_4 ($\Omega \text{ cm}^{-2}$)	R_6 ($\Omega \text{ cm}^{-2}$)	C_3 (F cm^{-2})	C_5 (F cm^{-2})	α
-1325	0.0215	0.139	0.0085	0.0939	0.053	0.013	0.59
-1283	0.0613	3.19	0.0370	0.0941	0.065	0.014	0.63

$$Z_c = \frac{1}{C_3 \omega_0 (i\omega/\omega_0)^\alpha} \quad (5)$$

The equivalent circuit thus defined was expressed mathematically by a transfer function and the parameters involved were calculated by trial and error to fit the course of the measured impedance characteristics. The data thus obtained are given in Table 1. The results can be discussed as follows.

When the zinc electrode is discharged, the Warburg diffusion impedance increases about three times owing to diffusion hindrance in the dense ZnO layer, while the electrolyte resistance, R_6 , remains constant. The resistance R_2 grows enormously as a result of thickening of the ZnO layer, the charge-transfer resistance, R_4 , increases similarly to the Warburg impedance, and the two capacities are only altered a little. The values of C_5 are lower than C_3 , ZnO being a semiconductor.

The measured and calculated impedance characteristics are shown in Figs. 1 and 2. It can be seen that the agreement is excellent. Thus, it seems that the proposed equivalent circuit is adequate.

The values of C_3 and C_5 are little changed during discharge. It seems that the value of C_5 corresponds only to the capacity of a thin ZnO layer adjacent to the zinc surface. The value of C_3 is proportional to the surface area of zinc, which does not change appreciably when passing from the 'charged' state to the partly-discharged one.

Conclusions

In comparison with partially-charged zinc electrodes, the Warburg diffusion impedance and the charge-transfer resistance increase considerably for fully-discharged electrodes, and the resistance of the ZnO increases enormously. Capacities corresponding to the porous zinc and ZnO, formed during the electrochemical process, change slightly. Probably, the restricted amount of the electrolyte in a hermetic cell affects little the impedance characteristics of the charged zinc electrode.

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