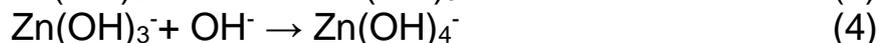
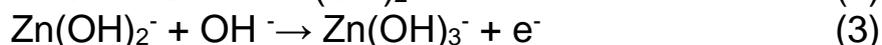


THE DENSITY GRADIENT THERMAL AGING MODEL OF THE ALKALINE Zn-Mn BATTERIES

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The processes of the primary alkaline Zn-Mn batteries thermal aging are investigated with electrochemical impedance spectroscopy. It is shown that during heating of the charged alkaline Zn-Mn battery zinc components are transported via the battery electrolyte. The homogeneous diffusion of ions was explained by using a density gradient model. This model is based on convective electrolyte flow as a result of changes in the density and volume of the battery electrolyte under thermal impact. The calculations of the impedance spectra of the primary alkaline Zn-Mn batteries established that the main element of the equivalent electrical circuits denotes to inhomogeneous diffusion and the density gradient is element of short Warburg.

It is well-known that in the zinc electrode compartment the electrode process consumes zincate ions and produces hydroxyl ions during charge; inversely, during discharge it produces zincate ions and consumes hydroxyl ions (density gradient model) [1]. This model is based on the Bockris et al studies of a zinc electrode in alkaline media and named B-mechanism [2]:



The active material formed moves away from the electrode edges and piles up towards the plate bottom and center [2]. The transport of zinc material leads to a reduction of the capacity and service life of the battery (in this thesis zinc material refers to all zinc species which entrain zinc, such as Zn, ZnO, Zn(OH)₂, K₂Zn(OH)₄, Zn(OH)₄²⁻, polymeric zinc species) [3]. Generally, diffusion and natural convection are considered to be relatively slow processes and are believed to be too slow to be responsible for the occurrence of electrode shape change [1]. From the above experiments it is deduced that the electrolyte flow in the battery is the principal mode of material transport in the battery. During the battery

operation a composition of battery electrolyte changes continuously. Since the properties of the battery electrolyte (e.g. density, conductivity, viscosity) change markedly with varying solute concentration [1, 4], they must also change during the life of battery. If the concentration gradients and density gradients develop perpendicular to the zinc electrode surface, a solution layer adjacent to the electrode with a density which differs from the density of the bulk electrolyte arises. This layer can extend gradually from within the electrode matrix to close to the separator, depending on the progress of the cycling process, the geometry of the cell and the properties of the electrolyte [1]. It is important to know the temperature and concentration dependence of the specific electrical conductivity of the electrolyte (σ), in order to minimize the Ohm losses in an alkaline cell through the optimal design of the system. The conductivity of the commonly used potassium hydroxide (KOH) is well described from 0 to 100 °C and concentrations up to 45 wt% in the work [5]. The presence of a porous structure activates the immobilization of the liquid electrolyte by capillary forces. In this case, the reduced free volume for the liquid electrolyte is expected to result in a decrease in conductivity, and by that to an increase in Ohm losses. Contrariwise, passivation and densification of the zinc electrode have been identified as the principal causes for the poor life time of the battery [1,6]. Dendrite deposits have a fern-like structure, and are formed during charge of the zinc electrode at potentials greater than about 80 mV [7]. The dendrites grow perpendicular to the zinc electrode in the direction of increasing zincate concentration. These dendrites, eventually, may short-circuit the cell making an abrupt end to a useful battery life. However, this problem has been largely overcome by improvements in separators and by additives to the electrode and electrolyte, which mitigate dendrite growth [8].

So the solution to battery state of health must come from a thorough understanding of the fundamental phenomena involved in the redistribution of the zinc material over the electrode. Therefore, the aim of this study is to elucidate the process and mechanism of battery state of health change with a model of the density gradient upon thermal impact which can account for the observed phenomena using impedance spectroscopy data.

Research methodology

Alkaline zinc manganese charged elements in AAA gross geometry (MN 2400) with a voltage of 1.5 V of the Duracell company were chosen as the samples to be tested. The impedance spectra were taken in a two electrode cell using an Autolab-30 electrochemical modular block (PGSTAT302N Metrohm Autolab) equipped with an FRA (Frequency Response Analyzer) assembly unit within the range from 10^{-2} to 10^6 Hz.

The modular block was controlled by Autolab 4.9 according to the standard procedure with postprocessing in Zview 2.0. The electrochemical reactions were simulated by the equivalent circuits method.

The specified temperature measurement conditions were provided by an electromechanical medium temperature thermostat (Ukraine) with temperature variance in ± 1 °C. The initial (charged) samples were tested on thermal exposure for 30 min in the temperature range 10 - 80 °C with a step of 10 °C.

Results and Discussion

It is well-known that the appearance of zinc salts changes the density of the electrolyte and forms the conditions of the density and concentrations gradients generation [1]. Conversely, temperature also changes the density of electrolyte [5]. So, all of these factors assist the creation of diffusion zones. Such zones are well modeled by the short Warburg element, which simulates the impedance of linear diffusion process in a homogeneous layer with finite size (Table 1) and correspond to the equation:

$$Z_{BW}(j\omega) = R_{ct} k_f (j\omega D_0)^{-1/2} th(j\omega \delta_N^2 / D_0)^{-1/2}, \quad (1)$$

where R_{ct} is the charge transfer resistance, k_f is the rate constant of oxidation reaction, D_0 is the diffusion coefficient of oxidant; δ_N is the thickness of the Nernst diffusion layer.

The singularity of this element is that it approaches the finite real value at a frequency $\omega \rightarrow 0$ (property of the constant electric current) and demonstrates the equivalence between the bounded diffusion and the finite conductivity.

The model element W_s has three poles. This means that it has an input, an output, and a common zero, ideally having a complete symmetry. But, in practice, there is always a disbalance of symmetry, which is caused by violation of the equality of the currents at the input and output. Such deviations are modeled by two substitution schemes: T-like and P-like schemes. The T-scheme is modeled by a deflection of the electric current in the case of the appearance of counter currents, while the P-circuit characterizes the approximation to the linear process. The O(R) – scheme characterizes an ideal symmetric process. According to Eq. 1, such an element will be represented by a chain of two parallel branches: the branch of the symmetric and linear Warburg elements and the branch of double electric layers (Fig.1). Such layers are formed under diffusion inhomogeneity impact and characterized by the presence of the counter currents. Thus, the change in the resistance

values on the T-branch will characterize the inhomogeneous diffusion, and the change in the branch of Warburg elements characterizes the deviation from linearity in the presence of adsorption of the diffusing ions.

Table 1. Equivalent electrical circuits of the charged elements after thermal impact and the average calculated values of their resistances

T ⁰ C	R ₁	R ₂	L ₁ 10 ⁻⁷	W-P	W-T	W-R	Equivalent electrical circuits
15	0,21± 0,05	6,32± 0,05	3,16 ± 3 10 ⁻⁸	-	-	-	
30	0,18± 0,05	9,38± 0,05	4,81± 3 10 ⁻⁸	0,66± 0,07	0,20± 0,01	0,61± 0,01	
40	0,20± 0,05	8,20± 0,05	4,34± 3 10 ⁻⁸	0,82± 0,07	0,20± 0,01	0,65± 0,01	
50	0,26± 0,05	7,88± 0,05	4,25± 3 10 ⁻⁸	0,85± 0,07	0,20± 0,01	0,66± 0,01	
60	0,30± 0,05	7,49± 0,05	4,16± 3 10 ⁻⁸	0,90± 0,07	0,20± 0,01	0,67± 0,01	
70	0,20± 0,05	8,1± 0,05	4,14± 3 10 ⁻⁸	0,95± 0,07	0,20± 0,01	0,68± 0,01	
80	0,19± 0,05	8,2± 0,05	4,14± 3 10 ⁻⁸	0,98± 0,07	0,20± 0,01	0,70± 0,01	

In particular, formation of Warburg elements can result from the local electrical conductivity changing in the presence of components that increase or decrease the concentration of OH⁻ and ZnOH⁺ ions. Changes in the local ions concentrations are the function of two parallel processes: thermal activation of the salts dissociation and immobilization of the electrolyte on the surface of the conductive phase (in particular, graphite) [9]. It was reported [10] that the probability of KOH immobilization on the graphite surface is very high and in the temperature range up to 60⁰C it practically does not affect the value of electrical conductivity. So, elements of short Warburg can form due to the presence of diffusion in two electrolyte systems (free and immobilized), in the absence of electrode reaction at temperatures up to 60 °C.

In this case, electrolyte depletion should occur at a temperature above 50 °C [10] due to a decrease in the electrolyte volume. Such a decrease is due to the formation of potassium zincates and the adsorption of potassium hydroxide on the graphite surface. Thus, de facto at temperatures above 50 °C there is no liquid electrolyte in the

electrochemical system. The absence of electrolyte solution is characterized by an approximation of W-P values to 1.0 at constant values of W-T and monotonically increasing of W-R values (Table 1).

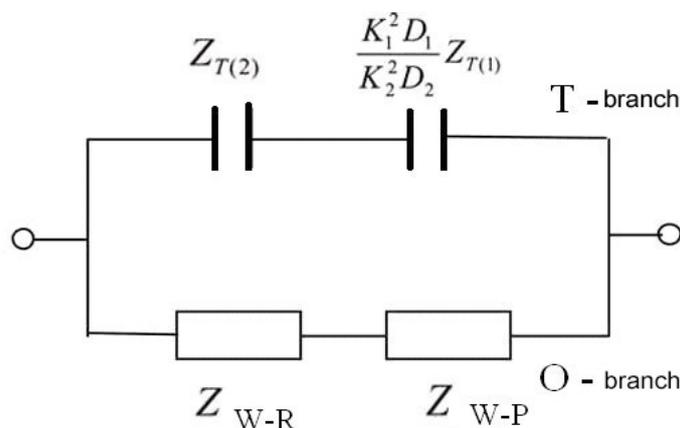


Fig.1. Equivalent electrical circuits of the inhomogeneous diffusion Warburg element

The presence of two diffusion types in such electrochemical systems enables the use of the density gradient model. This model is based on convective electrolyte flow as a result of changes in density and volume of the battery electrolyte and on following postulates: 1 - in the zinc electrode compartment the electrode process consumes zincate ions and produces hydroxyl ions during charge; 2 - since the properties of the battery electrolyte change markedly with varying solute concentration, they must also change during cycling and heating of the battery; 3 - concentration gradients and density gradients develop perpendicular to the zinc electrode surface; 4 - the diffusion coefficients of potassium and hydroxyl ions are considerably larger than that of zincate ions; 5 - separator strongly inhibits the migration and diffusion of zincate ions. As a consequence, the solution layer adjacent to the electrode with a density which differs from the density of the bulk electrolyte arises.

Conclusions

Using electrochemical impedance spectroscopy it was found that the thermal aging of the alkaline Zn-Mn batteries could be described by the density gradient model. The formation of density gradient is based on the changes of the local ions concentrations in two parallel processes: thermal activation of the salts dissociation and immobilization of the electrolyte on the surface of the conductive phase - graphite. This model is based on convective electrolyte flow as a result of changes in density and volume of the battery electrolyte under thermal impact. The main element of the equivalent electrical circuits denotes to inhomogeneous diffusion and the density gradient is element of short Warburg. It was found that the absence of electrolyte solution is characterized by an

approximation of W-P values to 1.0 at constant values of W-T and monotonically increasing of W-R values.

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