Estimation of the pressure in a hermetic Ni–Cd accumulator from its low-frequency impedance

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Abstract

The impedance characteristics of different hermetic Ni–Cd accumulators were studied in the frequency range 10^{-2}–10^{3} Hz during standing after charging to a pressure of 150 kPa. The pressure decreased linearly over several hours owing to oxygen reduction at the Cd electrode, and it was correlated with the low-frequency impedance of the accumulators. Based on this correlation, a method is proposed for the estimation of the pressure and rate of oxygen reduction in hermetic accumulators from the phase angle shift measured at 0.01 Hz.

Introduction

The dynamics of pressure changes during charge and discharge is an important characteristic of an hermetically sealed Ni–Cd accumulator, determining both the limits of its safe functioning and its energetical parameters. The pressure, P, in such an accumulator is determined by the equation [1]:

$$\frac{dP}{dt} = \frac{a}{4}(I^{O_2} - I_{O_2}) \quad (1)$$

where t denotes time, I^{O_2} and I_{O_2} are currents due to generation of oxygen at the positive electrode and to its ionization at the negative, $a = RT/FV_g$, V_g denotes free gas volume of the accumulator. It is obvious that $dP/dt > 0$ if $I^{O_2} > I_{O_2}$ and vice versa, hence, the slope of the barodynamic curve indicates the prevailing role of one of the two processes.

The transport of oxygen from the positive to the negative electrode proceeds by diffusion in the oxygen-saturated electrolyte and by transport through the gas phase; the rate-limiting step of the oxygen ionization is diffusion, through a thin electrolyte layer, to the surface of the cadmium electrode. Accordingly, the reduction rate of oxygen in a hermetically sealed

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Ni–Cd accumulator depends on the active surface area of the cadmium electrode and on the rate of oxygen diffusion. The former quantity depends on the state of charge of the electrode and on the morphology of cadmium oxyhydroxide, which blocks the active surface. The rate of oxygen diffusion depends on the diffusion coefficient and on the thickness of the electrolyte layer.

Transport of mass at the electrodes determines their impedance characteristics in the low frequency region (Warburg impedance). Therefore, a correlation is to be expected between the oxygen transport parameters at the fully charged Cd electrode (thickness of the electrolyte film, gas pressure) and the low-frequency impedance of the accumulator.

The present work deals with studies of hermetically sealed Ni–Cd accumulators during storage in the charged state; an attempt is made to elucidate the connection between their barodynamic and impedance characteristics.

Experimental

Most experiments were undertaken on hermetically sealed Ni–Cd accumulators of 90 A h capacity with sintered positive and rolled negative electrodes. The internal pressure was measured with a manometer. Impedance measurements were made on home-made equipment where the response, u, to a.c. current in the frequency range 0.01–1000 Hz was analysed to obtain the impedance components differing in their phase by $\varphi = \pi/2$. The output signal was represented in the form $u(t) = \Sigma f_k(u)\varphi_k(t)$, where $t \epsilon T$, $\varphi_k (k = 1,2,\ldots)$ are base functions, $f_k(u)$ is a functional depending on $\{\varphi_k\}$ and $u(t)$, and T denotes the time interval on which the mentioned representation is defined. Step functions were chosen as the base, allowing minimization of the measurement errors at a suitable ratio of the step parameters. The integration range depended on the frequency of the measuring signal, but it was not below 50 s. Since the integration duration was commensurable with the steady-state process time in chemical current sources, the impedance measurement reproducibility decreased with decreasing frequency from $\pm 1\%$ at 1000 Hz to $\pm 10\%$ at 0.01 Hz. The a.c. measurement signal of 1 A ensured an accumulator response not exceeding 3 mV over the whole frequency range.

Impedance measurements of 225 mA h capacity hermetic Ni–Cd cells were made on a Solartron 1250 frequency response analyser coupled with a Solartron 1286 interface in the range from 0.01 to 10^4 Hz.

Results and discussion

It follows from studies of the impedance characteristics of hermetic Ni–Cd accumulators of 90 A h capacity [2] that the diffusion control region on the impedance diagram corresponds to the frequency range 10–0.01 Hz.

A typical time–evolution diagram, during standing of an accumulator charged to a pressure of 150 kPa, is shown in Fig. 1. The change in the impedance diagram is related to the decrease of pressure in the accumulator; the real component changes only slightly (at a given frequency), the imaginary one increases monotonically with time. At low pressures, the diagram approaches a straight line with a slope of 55°.

The state of the hermetic Ni–Cd accumulator during standing is best reflected by the imaginary component at 0.02–0.01 Hz or by the phase angle. At higher frequencies the sensitivity of the method is lower, at lower frequencies the measurement takes a longer time. The time evolution of the pressure and phase angle at 0.01 Hz for two charged accumulators with different rates of gas recombination is shown in Figs. 2 and 3.

During the initial standing period (0.5–1.5 h), and during overcharge, the oxygen evolution at the positive electrode prevails over its ionization at the negative, as can be seen from Fig. 2. Later (up to 10 h), when the decomposition rate of the higher oxides of nickel decreases considerably, the pressure decrease from 150 to 70 kPa is nearly linear. This corresponds to the linear changes of the impedance characteristics with time (Fig. 2) and with pressure (Fig. 3). The latter dependence can be elucidated by assuming that the changes in the low-frequency impedance take place during the period determined mainly by processes at the Cd electrode.

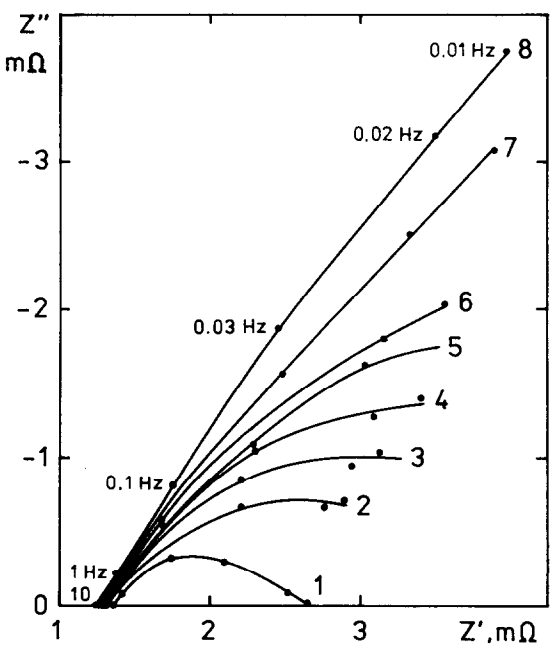

Fig. 1. Impedance characteristics, changes during standing, of charged hermetic Ni–Cd 90 A h accumulators. Time elapsed: 1, zero; 2, 0.7 h; 3, 1 h; 4, 2 h; 5, 2.5 h; 6, 4 h; 7, 15 h; 8, 84 h.

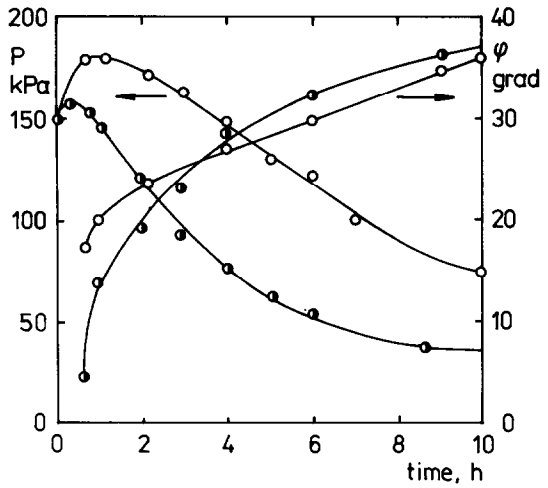

Fig. 2. Changes of pressure, P, and phase angle, φ, with time at 0.01 Hz, of charged, hermetic Ni–Cd 90 A h accumulators with different oxygen reduction rates.

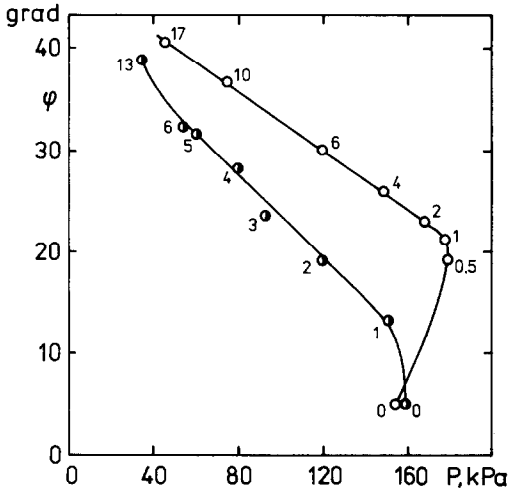

Fig. 3. Dependence of phase angle, φ, at 0.01 Hz, on the pressure, P, in hermetic Ni–Cd 90 A h accumulators with different oxygen reduction rates. Standing time given in hours.

To prove this supposition, we studied a non-hermetic cell prepared from the same accumulator's electrodes and assembled under similar conditions to those met with in production. The capacity of the positive electrode was 3.2 A h, that of the negative electrodes 12 A h. It was confirmed that changes in the cell's impedance characteristics on standing, after charging to 110%, ceased after 1.5 h, which supports our assumption.

Further impedance measurements were made on a model hermetic, 225 mA h Ni–Cd accumulator with net-type electrodes and with a built-in Hg/HgO reference electrode [3]. Time changes in the impedance diagram were

only observed in the diffusion control region (10–0.01 Hz), and they were similar to those mentioned above with the 90 A h accumulator, as may be seen from Fig. 4. The ohmic resistance, corresponding to the electrolyte between the electrodes and in the pores, decreases, which is probably due to changes in the electrolyte content. Time changes in the Cd electrode characteristics are significant only in the frequency range 0.1–0.01 Hz.

The change in the phase shift of the Cd electrode at 0.01 Hz over 7 h, after charging the accumulator to 30 kPa, is shown in Fig. 5. The internal pressure gradually decreased and reached zero after 2 h. It can also be seen that the phase shift of the positive electrode at 0.01 Hz stabilised after 0.5 h, probably because its charge state was lower than in the 90 A h accumulators mentioned above. The phase shift change of the negative electrode is linear over 2 h; as soon as the pressure drops to zero, the rate of change of the phase shift decreases. The impedance characteristic of the Cd electrode stabilised 6 h after charging ended.

In the following cycle, after a new charge, the oxygen pressure dropped markedly as a result of the induced dehermetization. This caused a stepwise increase in the phase shift — evidence of a correlation between the imaginary component of the impedance and the partial pressure of oxygen.

The foregoing results allow us to elucidate the impedance characteristic changes of hermetic Ni–Cd accumulators, on standing after charging, as follows. The imaginary component increase in the diffusion control region of the time interval from 1 to 10 h is related to the decrease in the depolarizing

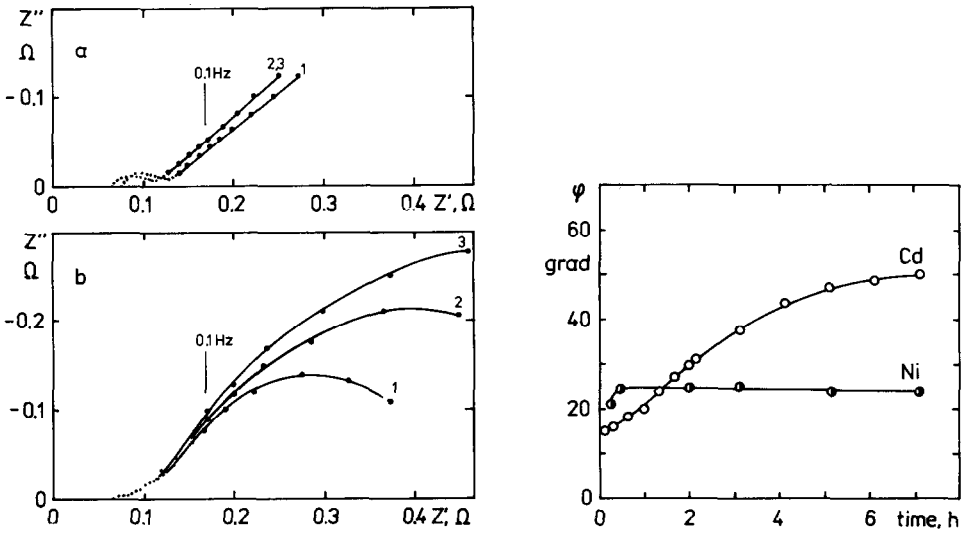

Fig. 4. Impedance characteristics changes with time, of charged, hermetic Ni–Cd 225 mA h accumulator electrodes. (a) Positive electrode: 1, 115 kPa, 0.5 h; 2, 75 kPa, 3.0 h; 3, 30 kPa, 5.5 h. (b) Negative electrode: 1, 105 kPa, 1.0 h; 2, 65 kPa, 3.5 h; 3, 25 kPa, 6.0 h.

Fig. 5. Changes of phase angle, φ, with time, at 0.01 Hz, of hermetic 225 mA h Ni–Cd accumulator electrodes charged to 30 kPa.

action of oxygen caused by the drop in its partial pressure. Indeed, during passage of a low-frequency a.c. current, the concentration drop in the potential-determining ions results in a polarization increase in the cathodic half-wave, and a polarization decrease in the anodic half-wave, the potential course being retarded with regard to the current. During cathodic polarization of the Cd electrode, the potential does not correspond to the actual concentration of the CdO_2^{2-} ions: it is considerably lowered by the oxygen reduction. Therefore, the effect of oxygen in the electrolyte is equivalent to a concentration increase of CdO_2^{2-} ions, resulting in a decrease in the Warburg impedance.

If, by contrast, the partial pressure of oxygen drops, causing a decrease in its depolarizing effect, the Warburg impedance increases.

The depolarization of the Cd electrode by the diffusing oxygen, on standing, can be estimated from the equation

$$\Delta\eta_{O_2} = \frac{RT}{2F}\frac{S_{gp}\cdot i_{O_2}}{S_k\cdot i_{O,k}} \tag{2}$$

where $i_{O,k}$ denotes the exchange current of the Cd electrode, i_{O_2} the limiting diffusion current of oxygen, S_k the electrochemically active surface area of the Cd electrode, and S_{gp} the surface area of the gas pores.

The limiting diffusion current of oxygen is given as

$$i_{O_2} = \frac{2FD}{\delta} H_{O_2} P_{O_2} \tag{3}$$

where P_{O_2} denotes the partial pressure of oxygen, D is its effective diffusion coefficient, H_{O_2} is Henry's constant, and δ is the effective thickness of the diffusion layer of the electrolyte film in the pores.

The parameters in eqns. (2) and (3) are known from the literature and from experiments: $i_{O,k} = 10$ A m^{-2}, $D = 3\times10^{-9}$ m^2 s^{-1}, $H_{O_2} = 10^{-6}$ mol m^{-3} Pa^{-1}, $\delta = 10^{-5}$ m, $S_k = 10^6$ m^2 m^{-3}, $S_{gp} = 10^5$ m^2 m^{-3}. Thus, $\Delta\eta_{O_2} \approx 2\times 10^{-8} P_{O_2} = 0.002$ V for $P_{O_2} = 10^5$ Pa. This value is of the same order of magnitude as the response of the accumulator to the a.c. signal at the pressure indicated.

The rate of oxygen reduction at the Cd electrode, which can be characterized by the ratio of S_{gp}/S_k according to eqn. (2), has a direct influence on the impedance of the accumulator. Observations made on a set of six, 90 A h accumulators with widely differing rates of gas recombination showed the possibility of evaluation of the accumulator characteristics. Selected data from barodynamic and impedance measurements of these accumulators, obtained during standing after charging to 150 kPa (i.e., about 120% of the capacity), are given in Table 1. The data can be correlated by the empirical equations $P_3 = 230 - 13\ \Delta\varphi$ and $\Delta P = 30 - 8\ \Delta\varphi$. Thus, the gas recombination characteristics in the accumulator can be estimated.

The method of evaluation of the pressure in the accumulator, and of its changes from the impedance characteristics, were verified during storage of a set of hermetic Ni–Cd accumulators of various constructions and manufacturing methods and of capacities ranging from 0.45 to 120 A h.

TABLE 1

Time changes of pressure, P, and phase angle, φ, at 0.01 Hz during storage of charged, sealed Ni–Cd accumulators of 90 A h capacity

Accumulator no.	Pressure (kPa)			Change in accumulator characteristics during storage for 1–3 h	
	P_{max}	P_1 (after 1 h)	P_3 (after 3 h)	ΔP (kPa)	$\varphi_{0.01\ Hz}$ (grad)
1	180	180	160	−20	5.5
2	170	160	145	−15	7
3	165	150	100	−50	10
4	160	145	95	−50	11
5	155	140	70	−70	12
6	155	130	60	−70	12.5

Disregarding variations of the measuring time interval, the method can be recommended for all the accumulator types.

Conclusions

A correlation was found between the oxygen partial pressure in charged hermetic Ni–Cd accumulators and their low-frequency impedance. This correlation is due to depolarization of the Cd electrode by oxygen.

Based on this finding, a method was proposed for estimation of the oxygen partial pressure and gas recombination rate in hermetic Ni–Cd accumulators from their low-frequency impedance in the charged state during standing.

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