Pressure build-up in aluminium electrolytic capacitors under stressed voltage conditions

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The internal gas evolution in aluminium miniature electrolytic capacitors exposed to stressed current and temperature conditions has been measured. The gas evolution is controlled by two competitive processes: hydrogen generation at the cathode and reduction of the depolarizers added to the electrolyte. The kinetics and efficiency of these reactions have been determined from measurements of the gas evolution for different temperatures and different currents through the capacitors.

1. Introduction

Aluminium electrolytic capacitors have been widely used in electronic circuits because they exhibit a very high capacitance per unit volume. However, they sometimes present problems during their working life such as leaking of the electrolyte through the seal and occasionally even explosions. These problems are usually prevented by careful life tests in which the capacitors are subjected to the nominal voltage V_N at high temperatures (about $100°$ C) for a 1000-h period. Unfortunately, this long lasting test yields little information about the origin of the failure mechanisms of the capacitors.

Previous dielectric measurements in aluminium electrolytic capacitors have shown a substantial increase in the equivalent series resistance (ESR) when they are subjected to high voltage conditions, i.e. to voltages higher than V_N. This increase in the capacitor ESR has been attributed, among other effects, to the electrolyte chemical degradation [1]. In this paper we further study the electrolyte degradation process by measuring the pressure increases in the interior of the capacitors induced by high voltages and temperatures up to $80°$ C. It is known that the increase of the internal pressure in wet electrolytic capacitors is due to hydrogen evolution at the cathode [2, 3]. In order to partially avoid a dangerous build up in pressure,

several reactive agents, termed depolarizers in the capacitor industry, are added to the electrolyte. Although the depolarizer plays an important role in preventing the evolution of hydrogen, there is a lack in the literature of systematic studies on their efficiency for hydrogen absorption.

2. Experimental details

Aluminium electrolytic capacitors of the miniature type were manufactured under standard specifications. The electrolyte consisted of a solution of boric, adipic and phosphoric acids in ethylene glycol, with picric acid (0.01 M) and p-benzoquinone (0.05 M) added as depolarizers. The resulting electrolyte presented a resistivity of about $80\,\Omega$ cm and had a pH of 5.1. The pressure inside the capacitors was monitored by a conventional U-shape manometer made from a capillary glass tube (diameter 0.8 mm) filled with distilled water. This manometer configuration permitted the measurement of pressure changes of less than 0.1 mm Hg above the atmospheric pressure. The manometer was hermetically connected to the interior of the capacitor by means of a capillary steel needle punched through the rubber seal.

In order to better relate the amount of gas generated to the electric charge passing through the capacitor, the experiments were performed
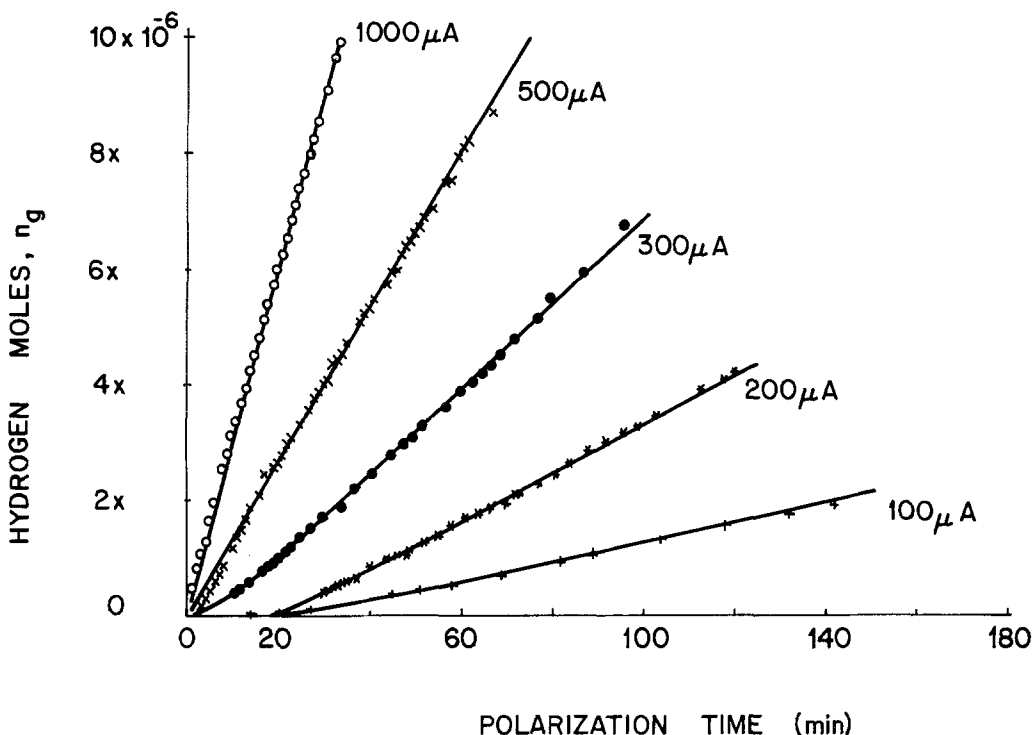
Fig. 1. Number of moles of gas evolved versus polarization time for different constant currents for 47 μF/40 V miniature capacitors.

at a constant current provided by an operational power supply (Kepco-OPS-2000). The currents applied to the capacitors were in the range 100–1000 μA, which are substantially larger than the capacitor leakage current and therefore enhanced the gas evolution phenomenon. The experiments were carried out at room temperature (20° C) and also at temperatures in the range 20–80° C with the purpose of investigating the behaviour of the capacitors under stressed working conditions.

The number of moles of gas, n_g, generated at a temperature T during the polarization of the capacitors can be calculated from the formula

$$n_g = \frac{P_0 V_d + P_m (V_m + V_d)}{RT} \quad (1)$$

where P_0 and P_m are the atmospheric and manometer pressures respectively, V_m is the empty volume of the capacitor–manometer system, V_d is the change in volume due to the displacement of the water column and R is the ideal gas constant.

3. Results

The amount of gas generated in moles (n_g) is shown in Fig. 1 as a function of time (t) for several values of the current through a 47 μF/ 40 V capacitor at room temperature. Similar results were also measured in other miniature capacitors (capacitance, 100 μF; nominal voltages, 25 and 40 V). As previously observed [4], n_g always increases almost linearly with time, although near the origin the slope increases slightly until it reaches a constant value. It can also be appreciated in Fig. 1 that the rate of increase of n_g is greater as the current increases. It is observed that for low polarization currents (below about 100 μA) the gas evolution rate is close to zero.

Experiments at different temperatures at a constant current of 500 μA were also carried out on several capacitors. Fig. 2 illustrates the typical behaviour of a 100 μF/25 V capacitor in the 22–76° C temperature range. An increase of the temperature in the capacitor generally
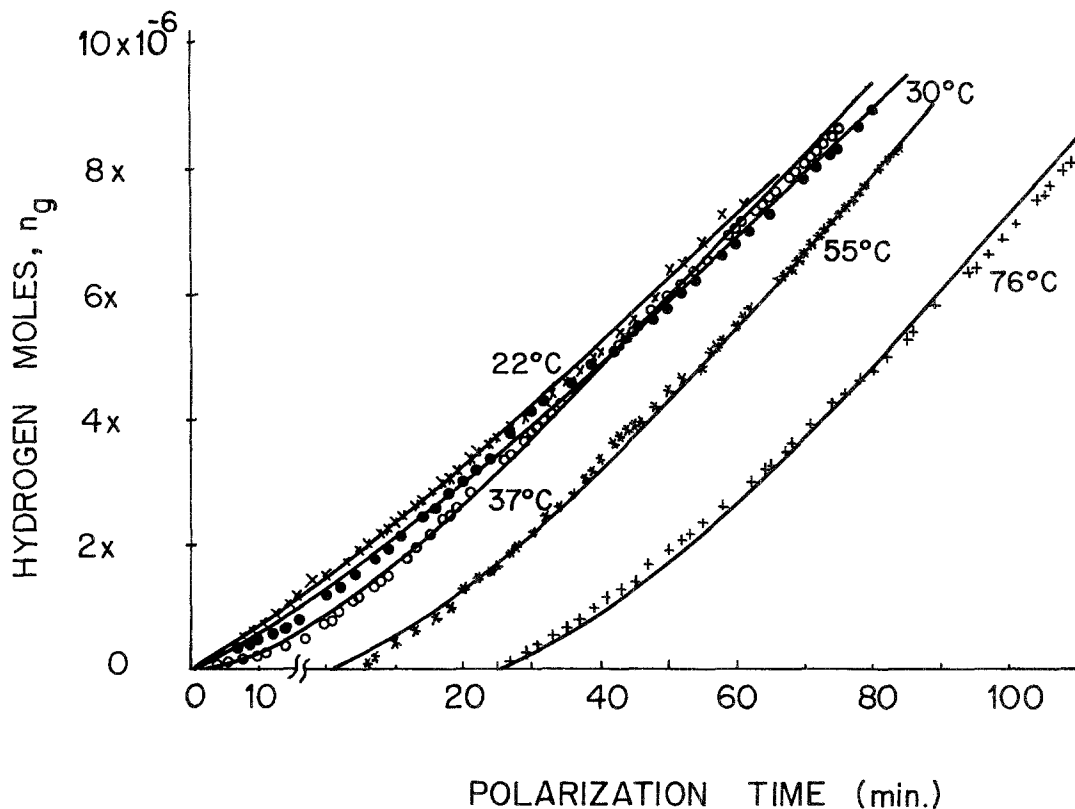
Fig. 2. Number of moles of gas evolved versus polarization time for different constant temperatures and $I = 500\,\mu A$ for $100\,\mu F/25\,V$ miniature capacitors. Notice that the time scale has been displaced for the 55 and 76° C curves. Solid lines represent Equation 3.

produces a reduction in the gas evolution, displacing the n_g versus t curves towards longer times. Consequently, the characteristics for 55 and 76° C show an induction time below which no gas evolution could be detected. The influence on n_g of the current at a constant temperature of 80° C has been measured and represented in Fig. 3 for the $100\,\mu F/40\,V$ capacitors. The results clearly show a decrease of the induction time when the current through the capacitor increases.

4. Discussion

4.1. Room temperature experiments

The results of Fig. 1 have been interpreted along the lines of our previous model on the gas generation in aluminium miniature electrolytic capacitors subjected to stressed electrical conditions [4]. According to this model the internal

production of gas is controlled by two competitive reactions: (i) hydrogen generation at the cathode following Faraday's laws, as proposed by Burger and Wiswanathan [2], and (ii) hydrogen reaction with the depolarizer according to a thermally activated process. We will further assume that the reduction reaction of the depolarizer follows first order kinetics. This assumption contrasts with the zero order kinetics proposed formerly [4] but it is a more realistic approach and gives a better fit to to the experimental results.

Representing the total number of moles of the depolarizer by n_d and the number of moles reacting with hydrogen during time t by $n(t)$, and assuming first order kinetics for the gas reaction, one obtains the equation

$$n(t) = n_d[1 - \exp(-kt)] \qquad (2)$$

where k is the rate constant for the absorption reaction. From this result, the amount of gas
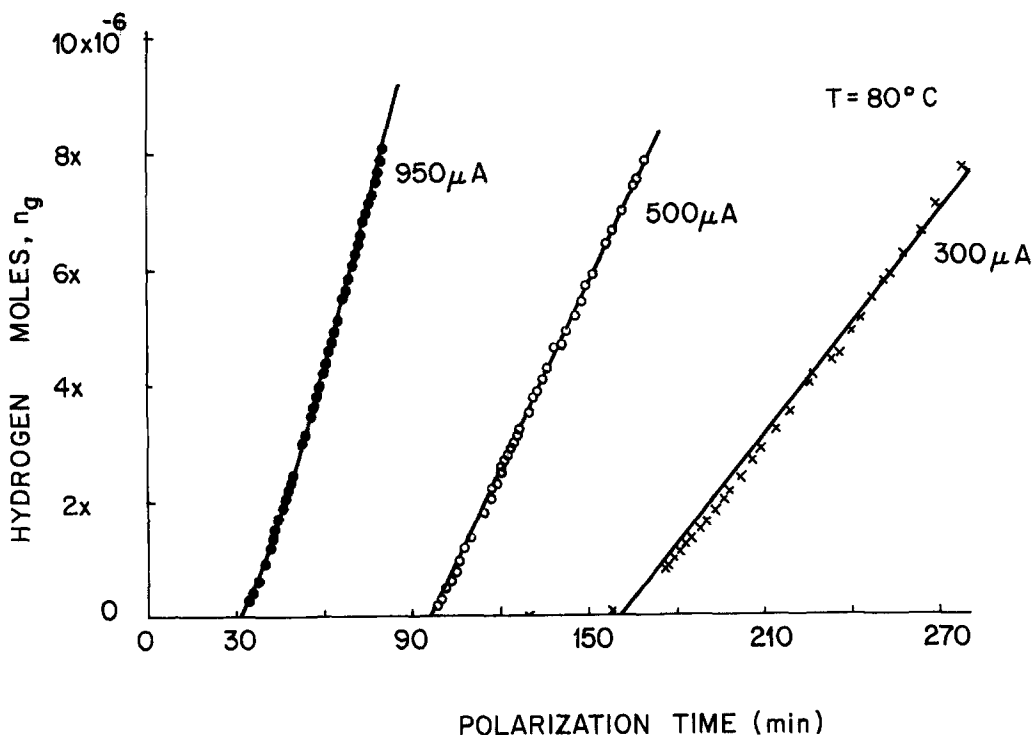
Fig. 3. Number of moles of gas evolved versus polarization time at 80° C for different currents for 100μF/40 V miniature capacitors. Solid lines represent Equation 3.

evolved measured by the manometer for a current density, i, through the capacitor is given by

$$n_g = Kit - n_d[1 - \exp(-kt)] \qquad (3)$$

where the first term gives the hydrogen production at the cathode according to Faraday's laws at a constant rate of K moles per unit charge density. For long polarization times, Equation 3 can be approximated by

$$n_g = Kit - n_d \qquad (4)$$

which has been used in our previous analysis of the gas evolution [4]. Thus, from the asymptotic value of the slope of the curves of Fig. 1, an approximated value of the constants K and n_d can be obtained. From these approximate values, the parameters K, n_d and k in Equation 3 were calculated by means of a least square fitting of this equation to the results of Fig. 1. The solid lines in this figure represent the theoretical curves obtained by this method.

The mean values of n_d and k drawn from this fitting for the 47 μF/40 V capacitor are 1.0 $\times$ 10^{-6} mol and 1.5 $\times$ 10^{-3} s^{-1}, respectively. The

gas generation rate, Ki, has been plotted in Fig. 4 as a function of the current density giving, as expected, a straight line. For comparative purposes, the values for the 100 μF/40 V capacitor using a similar analysis are also represented. From this graph, approximately the same value of $K = 8.3 \times 10^{-5}$ mol cm^{-2}C^{-1} is obtained for both capacitors. The intercept of the straight line with the abscissa, $\approx 3\,\mu$A cm^{-2}, represents the current density consumed in secondary reactions, i.e. that part of the current not taking part in the gas generation process [5].

The value of the number of moles of the depolarizer for different capacitors is given in Table 1. A linear increase of n_d with the cathode

Table 1. Calculated values of n_d for I = 500 μA in different capacitors

Capacitor (μF/40 V)	Cathode area (cm²)	n_d (mol)
47	16.65	1.0 $\times$ 10^{-6}
100	22.05	1.4 $\times$ 10^{-6}
100	32.30	2.0 $\times$ 10^{-6}
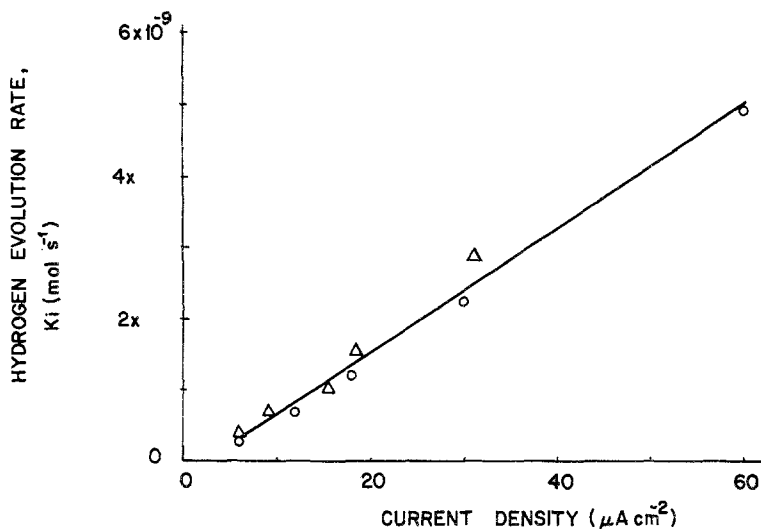
Fig. 4. Hydrogen evolution rate as a function of the current density for the $47\,\mu F/40\,V$ and $100\,\mu F/40\,V$ capacitors. O, $47\,\mu F/40\,V$; △, $100\,\mu F/40\,V$.

surface area of the capacitor is observed, suggesting the control of the absorption reaction by the cathode.

The calculated values of n_d can be compared with the number of moles of the depolarizer contained in the capacitor. For example, the $100\,\mu F/40\,V$ capacitors with a $0.5\,cm^3$ case can hold 5×10^{-6} and $25 \times 10^{-6}\,mol$ of picric acid and benzoquinone, respectively. The reduction reactions at the cathode for these compounds are [6, 7]:

$$\text{(5)}$$

$$\text{(6)}$$
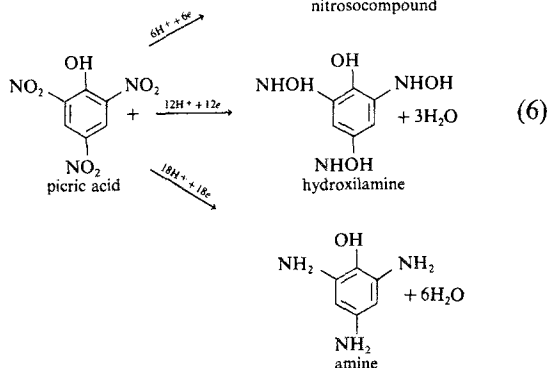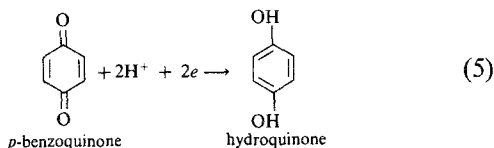
According to the above reactions, p-benzoquinone in the electrolyte can react with a number of protons equivalent to $25 \times 10^{-6}\,mol$ of hydrogen. As for the picric acid, it should react with the equivalent of $30 \times 10^{-6}\,mol$ of hydrogen if one assumes, as a first approach, that the three reaction products of its reduction are equally probable [6]. Therefore, the depolarizers in the electrolyte should be able to prevent the formation of up to $55 \times 10^{-6}\,mol$ of hydrogen. Comparing this value to the value of n_d from Table 1 for this capacitor, i.e. $n_d = 2.0 \times 10^{-6}\,mol$, it is concluded that even after the reduction reaction is accomplished, there remains about 96% of the depolarizer molecules inactive at room temperature. This fact, along with the above mentioned increase of n_d with the cathode surface, suggests that the reduction reaction of the depolarizer is controlled by the adsorption steps of the depolarizer molecules on the cathode surface.

4.2. High temperature experiments

In aluminium anodization experiments, increasing temperatures give rise to a greater depolarizer efficiency [3] and consequently to larger values of the induction time, i.e. the minimum time of polarization necessary to detect gas evolution. From Equation 3 the induction time, t_{ind}, will satisfy the condition

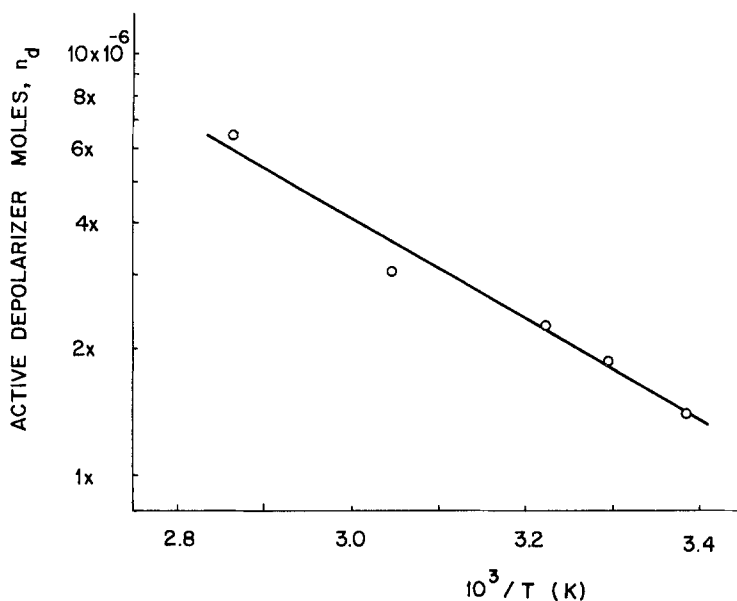$$Kit_{ind} \leqslant n_d[1 - \exp(-kt_{ind})] \qquad (7)$$

Fig. 5. Temperature dependence of the number of the reacting depolarizer moles in the hydrogen absorption process.

Evidence of this effect in the miniature capacitors can be obtained from Fig. 2 since as the temperature rises the slope of the curves near the origin steadily decreases, becoming zero at $T \approx 37°$ C. From this temperature upwards, the n_g versus t curves intersect the horizontal axis at longer times revealing the existence of an induction time in the temperature range.

The fitting procedure previously described has also been applied to the curves of Fig. 2 yielding the values of n_d and Ki shown in Table 2. The temperature dependence of n_d suggests a thermally activated reduction reaction [4], expressed by the equation

$$n_d = n_0 \exp (-\Delta E/kT) \qquad (8)$$

From the Arrhenius plot of Fig. 5, an activation energy $\Delta E = 6.05 \, kcal \, mol^{-1}$ is obtained, which probably corresponds to the adsorption step of the depolarizer molecules at the surface of the cathode.

From the results of Table 2, an increase of the slope values, Ki, with the temperature of the capacitors is also observed. In order to obtain a further insight into the influence of temperature on the constant K, some measurements of n_g were performed at a constant temperature whilst varying the current. Fig. 3 shows experimental results for the $100 \, \mu F/40$ V capacitors at $80°$ C and gives the number of moles of measured

hydrogen n_g as a function of the polarization time for three different currents. At this relatively high temperature, only the linear variation of n_g vs t curves corresponding to Equation 4 is observed. Following the previous analysis one obtains a constant value of $n_g = 10.6 \times 10^{-6} \, mol$. This value of n_d implies that even at $80°$ C about 84% of the depolarizer in the electrolyte is not reduced. Similarly, from the slopes of the curves in Fig. 3, a value of $K \cong 1.3 \times 10^{-4} \, mol \, cm^{-2} C^{-1}$ is calculated. In this respect, it is interesting to point out that, although the gas production efficiency increases with temperature, it does so at a rate smaller than the increase in the reduction rate by the depolarizer.

5. Conclusions

The internal gas evolution in miniature aluminium electrolytic capacitors, subjected to

Table 2. Variation of n_d and Ki with temperature for the $100 \, \mu F/25$ V capacitor

T (°C)	Ki (mol sec⁻¹)	n_d (mol)
22	1.78×10^{-9}	1.43×10^{-6}
30	1.79×10^{-9}	1.90×10^{-6}
37	1.94×10^{-9}	2.30×10^{-6}
55	2.58×10^{-9}	3.10×10^{-6}
76	5.45×10^{-9}	6.55×10^{-6}

stressed voltage and temperature conditions, is controlled by two competitive processes: (1) gas generation at the cathode following Faraday's laws, and (2) reduction of the depolarizer by means of a reaction (with the protons in the electrolyte) of small efficiency and approximately first order kinetics. Both reactions are favoured by the temperature, especially the second, which displays a thermally activated reaction rate. As a consequence of this, the gas evolution gets smaller when the capacitors operate at high temperatures. This effect gives rise to an induction time so that, at high temperatures, no gas evolution is observed for times shorter than the induction time.

Acknowledgements

References

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