Oxygen evolution during recharging of positive nickel oxide sinter electrodes

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Oxygen evolution during anodic oxidation of positive nickel oxide electrodes is of theoretical and practical interest both for open and sealed storage batteries. The gas volume produced on positive sinter electrodes during the charging operation has been plotted as a function of time, using a recorder. The influence of the anodic current and/or of the electrolyte temperature on the charging efficiency is discussed. The results permit the deduction of the optimum combination of charging parameters which are characterized by minimum parasitic oxygen formation. A small but continuous gas formation can be observed after the electrode is charged to about 50% capacity using charging currents of the order of the 1 hour rate at ambient temperature. At higher temperatures the beginning of gassing is shifted toward lower charge levels, e.g. at 40°C it already begins at a charge of about 17%. Furthermore the gas volume, which is evolved during charging to identical levels, was found to increase with increasing temperatures and decreasing current density. The described phenomenon can, at least in part, be explained by the decomposition of higher nickel oxides. The decomposition rate was shown to depend on charging time, charging current and temperature.

Introduction

During the charging of an alkaline storage battery, oxygen evolution begins at the positive electrode even before all of the active mass has been electrochemically oxidized. The beginning of gassing and the amount of gas evolved, depends, amongst other things, upon the system under consideration, the electrode, the electrolyte temperature and concentration as well as the charge current. In the present study oxygen evolution has been investigated in particular with respect to the magnitude of the charge current and the electrolyte temperature. In the course of this work it has been necessary to derive simple relationships which can be straightforwardly applied to technological practice. The theoretical treatment has therefore been modified to take account of this. First, however, we describe the automatically recording apparatus, which was used for the determination of oxygen, formed while the anode was under load.

Apparatus for oxygen measurement

Fig. 1 shows a schematic representation of the apparatus used in these investigations. A positive nickel sinter electrode foil (d) is placed in a transparent plastic container and is charged using over-dimensioned, discharged, cadmium sinter electrodes (c). The oxygen which is formed is released through the glass capillary (a). The escaping gas bubbles cause intensity changes in the coloured liquid (b) which are registered by a photocell as intensity changes of a lightbeam. The height of the liquid column above the capillary affects the bubble volume and thus the resolution of the apparatus. Therefore the liquid level has to be kept constant. The escaping gas bubbles

a = capillary tube
b = coloured fluid
c = counter electrode
d = working electrode
e = separator
f = constant current generator
g = reference electrode (Hg/HgO)
h = heating
k = phonometer
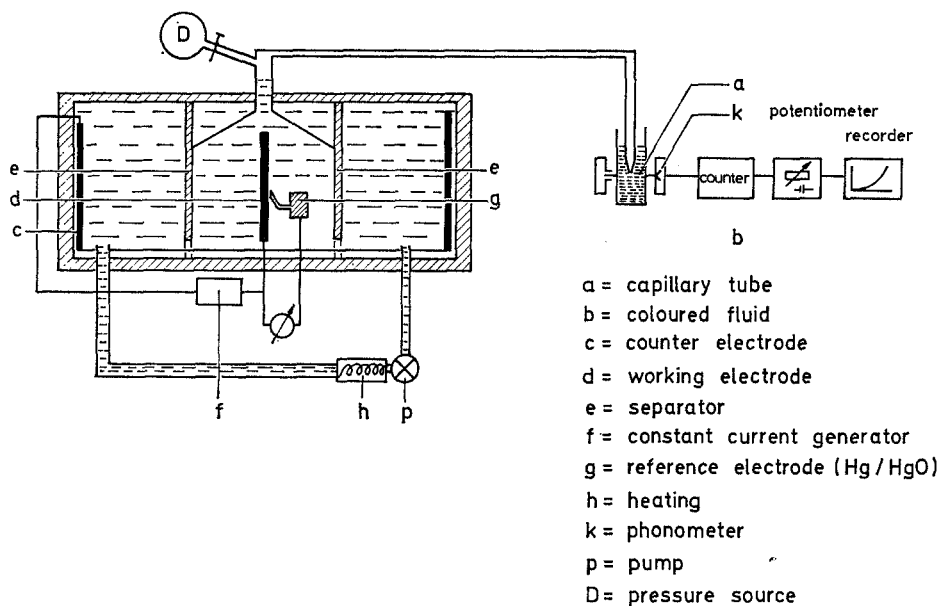p = pump
D = pressure source

Fig. 1. Gas-flow recording system.

cause light intensity changes creating a voltage impulse in the detector which is then amplified. A counter registers the total number of the escaping bubbles. The amplifier also actuates a potentiometer through a relay and a mechanical reducing gear. With each escaping bubble the potentiometer is moved by Δh causing a voltage change ΔU at the corresponding potential divider. This voltage is recorded by a compensating recorder. From the potential/time diagram one can obtain the number of bubbles or the gas volume as a function of time.

The sensitivity of the system must be high, so that all the gas, even that remaining in the pores of the electrode, can immediately be registered. This requires that the pressure in the connecting system between test cell and capillary tube be increased by the amount of the hydrostatic pressure. It can most simply be achieved by means of the pressure ball (D), which permits the desired adjustment of the overpressure in the tube system. The system is then immediately at equilibrium pressure since the overpressure is compensated by the capillary.

Experimental errors are caused by the O_2 solubility in the electrolyte, especially at low charging currents. They can be eliminated by circulating an electrolyte which has been saturated with O_2 at the given temperature.

Applying Faraday's laws and considering the experimental conditions, the calibration of the system at a constant current of 200 mA and 20°C resulted in 104 impulses for each 100 mV voltage difference which are equivalent to 1394 mm^3 of oxygen. The volume of one gas bubble is then calculated to be 13·4 mm^3.

Measurements and discussion of results

A nickel sinter foil with an area of 20 cm^2 and 0·63 mm thickness was used as the positive test electrode. Activation was achieved by chemically impregnating the foil with 9·8 g of $Ni(OH)_2/dm^2$. The anodic oxidation of $Ni(OH)_2$ was achieved by galvanostatic methods using charge currents C/5 = 95 mA and 1 C = 480 mA at electrolyte temperatures of 0°C, 20°C, 40°C and 45°C.

Fig. 2 shows the evolved amount of gas at 480 mA and 40°C and the electrode potential as a function of time. The potential is measured versus a Hg/HgO electrode and with a KOH electrolyte of density ρ = 1·2 g/cm^3. The curve has the expected shape: up to 60 min charge time the potential changes only little, but it increases in the following 10 min where it reaches the final value of 570 mV. The first oxygen bubbles are formed after 10 min of charge time corresponding to about 17% of the
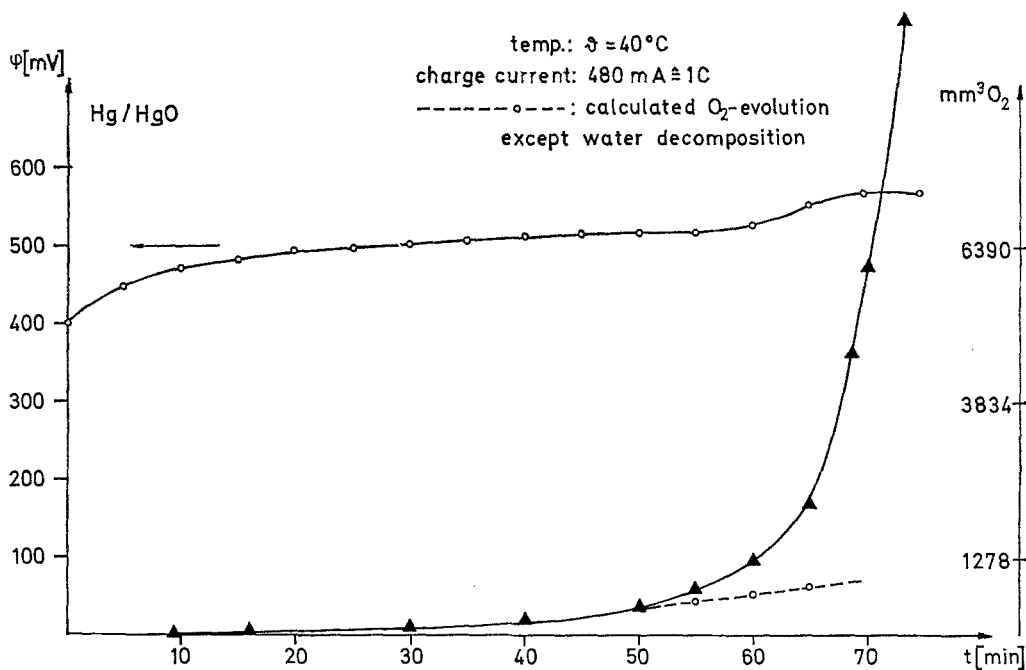
Fig. 2. Oxygen generation and potential v. charging time t.

capacity. The rate of O_2 evolution increases rapidly up to about 73 min. At longer times the change in rate decreases to very small values. From the record of the potential behaviour very little can be said about the beginning and the amount of gas evolution because the potential change is small over a wide range; therefore no practical interest exists. The potential in this region cannot be used for evaluating the efficiency of the charging process and the amounts of the gas losses.

The observed oxygen evolution is caused by more than one reaction which may occur simultaneously. An attempt will be made to demonstrate a functional connection between the gas evolution and the charging time. In order to accomplish this the various reactions which are responsible for the O_2 evolution have to be analysed.

First, the decomposition reactions of the higher nickel oxides have to be mentioned which are—upon further charging—masked by the oxidation of the OH-ions of the electrolyte. In the stationary case, with 100% Faraday-efficiency, the amount of oxygen registered is equivalent to the current.

The nickel oxides formed by anodic oxidation are designated in the following by the general formula NiO_x ($1 \cdot 3 \leqslant x \leqslant 1 \cdot 8$). Possible structural formulae for the oxidation products are discusssed in [1]. They will not be discussed in this work. From these studies and also from those of Conway [2] it is known that the higher nickel-oxides formed during charging, are unstable and that the O_2-liberation decreases the valency of nickel, which causes the potential to decay. Like Conway we also found a decay of the potential of charged positive electrodes during storage. Furthermore the rate of gas evolution during open circuit storage is comparable to that occuring during the charging period, provided no OH^- decomposition occurs. This is valid for charging times of up to 50 min for the conditions given in Fig. 2. In order to estimate the rate constants and the activation energies of these decomposition reactions, a kinetic analysis has been made and its solution will be compared with the experimental results. It may be mentioned that the exact compositions of the starting and end products are unknown.

The discharged electrode contains $Ni(OH)_2$, designated in the following by A. The anodic current oxidizes the active mass and the oxidation product B is represented by the nonstruc-

tural formula NiO_x ($1{\cdot}3 \leqslant x \leqslant 1{\cdot}8$). When the oxidation value is greater than $1{\cdot}33$, the product is unstable, O_2 evolution sets in and B changes to C. The nickel valency decreases. (The oxidation product depends strongly upon the electrode history and the charging conditions. Therefore it is of no advantage to use the reaction equation $Ni(OH)_2 \longrightarrow NiOOH + H_2O + e^-$ in the following discussion.)

Using the reaction scheme:

$$A \xrightarrow{k_0} B \tag{0}$$
$$B \xrightarrow{k_1} C$$
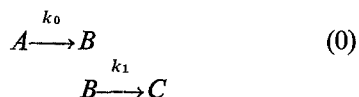
the amount of O_2 generated is equivalent to C when no OH^- decomposition occurs ($4\ OH^- \longrightarrow O_2 + 2H_2O + 4e^-$). For the reaction $A \longrightarrow B$, the concentration of product B is proportional to the current. The reaction $B \longrightarrow C$ is assumed to be a first order homogeneous reaction. We prefer to determine experimentally whether the decomposition of the higher nickel-oxides can be described by the above simple mathematical formulation. Referring to the reaction $A \xrightarrow{k_0} B$, the concentration change of the oxidized material (x) with time is proportional to the current, i.e.

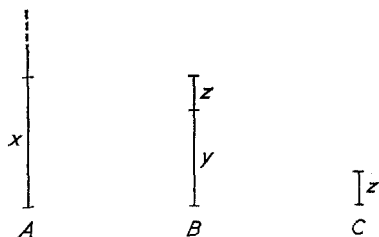$$\frac{dx}{dt} = k_0 I \tag{1}$$

or

$$x = k_0 . I . t + c' \tag{2}$$

with $c' = 0$
for $t = 0, x = 0$.

The second reaction $B \xrightarrow{k_1} C$ is assumed to be a first order reaction:

$$\frac{dz}{dt} = k_1 y \tag{3}$$

Scheme 1 indicates the amounts (x, y, z) of the reacting parts (A, B, C,)

x, y and z are related through the expression:

$$y = x - z.$$

From (3) it follows:

$$\frac{dz}{dt} = k_1(x - z) \tag{4}$$

By combining equations (1), (3) and (4) we obtain:

$$\frac{dz}{dt} = k_1 k_0 I t - k_1 z. \tag{5}$$

The result of this inhomogeneous first order differential equation describes the O_2 evolution as a function of time.

The homogeneous part has the solution

$$z(t) = C_1 e^{-k_1 t}. \tag{6}$$

We find by varying the constants: $C_1 = c(t)$

$$z(t) = c(t) e^{-k_1 t}. \tag{7}$$

If we differentiate this equation and substitute it into (5), we obtain Equation (8)

$$z = \frac{Ik_0}{k_1}\left[e^{-k_1 t} + k_1 t - 1 \right] \tag{8}$$

Expanding the exponential term of Equation (8) as follows:

$$e^{-k_1 t} = 1 - k_1 t + \frac{(k_1 t)^2}{2!} - \frac{(k_1 t)^3}{3!} \pm \cdots$$

it becomes:

$$z = \frac{Ik_0}{k_1}\left(\frac{(k_1 t)^2}{2!} - \frac{(k_1 t)^3}{3!} \pm \cdots \right)$$

and, since $k_1 t$ is for all reasonable values of t much smaller than 1, it is possible to neglect the higher power terms of $k_1 t$ and the equation simplifies to

$$z = \frac{Ik_0 k_1 t^2}{2}. \tag{8a}$$

Equation (8a) is simpler to use and the results are not more than 1–2% in error.

The amount of oxygen, formed during the decomposition of nickel oxides, is designated as z. This formulation is correct, when the amounts of oxygen measured at different times t_i are in agreement with those calculated from equation (8) or (8a). This will be the case if, for all experimental values at constant current, valid constants k_0 and k_1 can be found. Changes in

charging conditions require a modification of k_1. In addition it could be determined that for different charging currents the oxidation state of the nickel changes. For C/5 this level is determined as 3·08 and at 1 C we obtain 3·17 (KOH density $\rho = 1·20$ g/cm³). The main part of the oxidation product for C/5 is $\beta - NiOOH$ with a nickel valency of 3·0 whilst for 1 C more of the γ-phase [1] is formed, having a higher oxidation level and perhaps a different stability than the β-phase. Further studies are under way. These results demonstrate that k_1 is not a true constant but a function of the charging current. In the following example the constants k_0 and k_1 have been determined for 1 C only.

Determination of the constants k_0 and k_1

k_0 can be chosen to be dimensionless or equal to 1 if t (s), k_1 (1/s), I (A), and z (As) are being determined. The experimental value of z (mm³ O₂) can be converted into As using Faraday's law. The temperature effect is described with sufficient accuracy by the ideal gas laws.

For a charging current of $I = 0·48$ (A) at $\delta = 40°C$ one obtains $k_1 = (3·4 \pm 0·1) \times 10^{-6}$ (1/s) (1 As $\triangleq$ 66·5 mm³) (Fig. 2). The rate constant k_1 is constant up to 46 min. For times longer than that, k_1 is continuously increasing and the kinetic formulation becomes invalid. The reason for this is that in addition to the

decomposition of the nickel oxide, the oxidation of the OH⁻ ions of the electrolyte begins, which causes an additional oxygen evolution.

Fig. 2 also shows the calculated gas evolution for longer times, where the assumption has been made that all oxygen is due to the decomposition of nickel oxides only and that no water decomposition occurs. From the difference between these calculated values and the experimental curve one obtains the amount of O₂ which is due to the decomposition of water. For the determination of rate constants at different temperatures only those experimental values which do not include the decomposition of water can be used.

We have summarized the determined rate constants in Table 1.

Table 1

°C	$10^6 k_1$ [1/s]
45	4 ± 0·1
40	3·4 ± 0·1
20	2·4 ± 0·2
0	1·5 ± 0·2

Determination of activation energies for the decomposition of higher nickel oxides

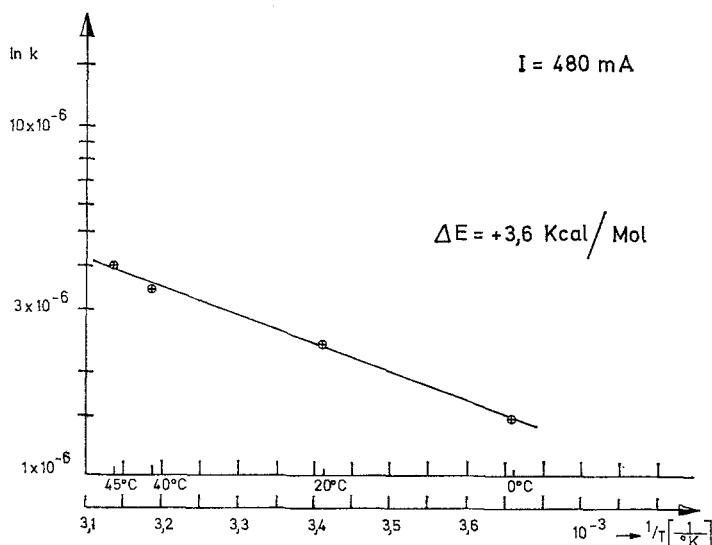With the rate constants known at different temperatures, one can derive an activation

Fig. 3. Arrhenius diagram for the decomposition of higher nickel oxides.

energy, using an Arrhenius plot. $k = A$ exp $(-(\Delta E)/(RT))$ gives the relation between the rate constant k and the temperature T (°K). Plotting the log of the rate constants (Table 1) v. $1/T$, a straight line is obtained. From the slope of this line one derives a ΔE of 3·6 kcal/mol, which may be attributed to the decomposition reaction (Fig. 3). Whether this assumption is correct or whether the activation energy should be attributed to diffusion processes remains to be seen.

O₂-evolution at various electrolyte temperatures

O₂-evolution at a charge current of 480 mA ($\cong$ 1C) and at various electrolyte temperatures is plotted in Fig. 4 against the capacity. The curves are similar to those in Fig. 2. It is interesting to note that the decomposition rate decreases with decreasing temperature. However, the water decomposition shifts to shorter times. Therefore the curves intersect. From the beginning of the charging process up to 460 mAh, the collected O₂ volumes are constant for all electrolyte temperatures. The efficiency of the charging process decreases with increasing temperature

up to a charge time of 58 min (460 mAh). For longer charging times, an increase is observed with increasing temperature. For low charging temperatures and short charging times, losses due to gassing are low, for longer charging times this relation is reversed. Decreasing the charging current to C/5, the losses due to gassing change considerably. A plot of the O₂-evolution v. charge capacity at 40°C is shown in Fig. 5. The first gas bubbles are formed after 30 mAh. It may be noted that during further charging the amount of O₂ collected at a charge current of C/5 is larger than that for a charge current of 1 C.

Calculation of the charge preserving current (CPC)

To compensate the capacity loss caused by the decomposition of nickel oxides, a charge preserving current can be calculated. According to Equation (5) a gas evolution rate $(dz)/(dt) = L$ is computed for the time t which is equivalent to a current (A). From (5) and (8) it follows:

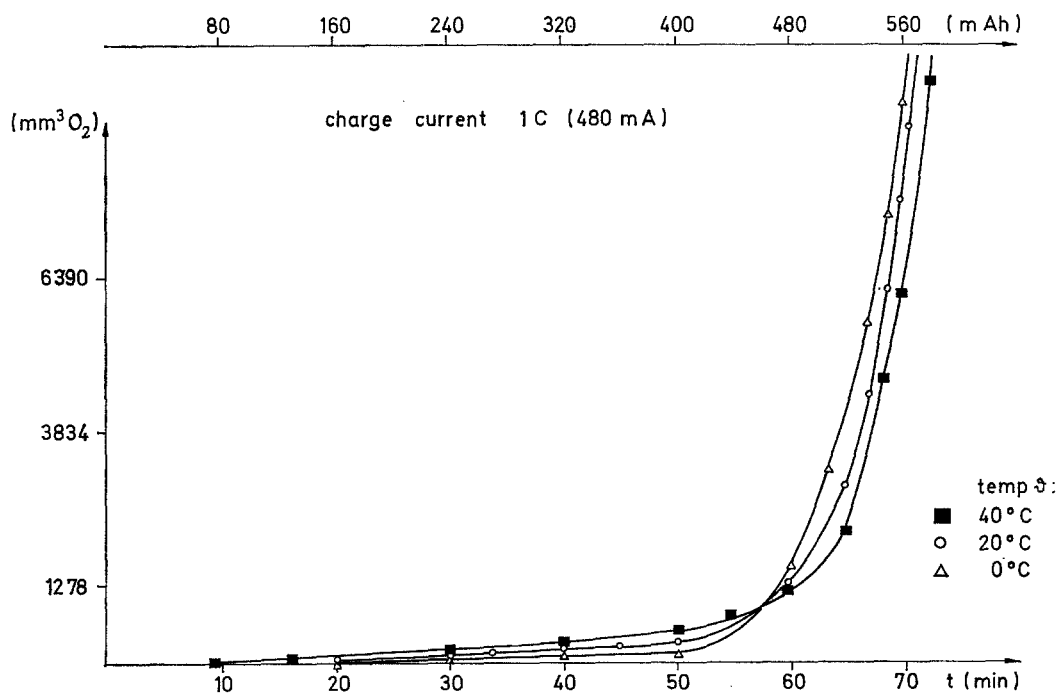$$\frac{dz}{dt} = L = I\,(1-e^{-k_1}) \tag{9}$$

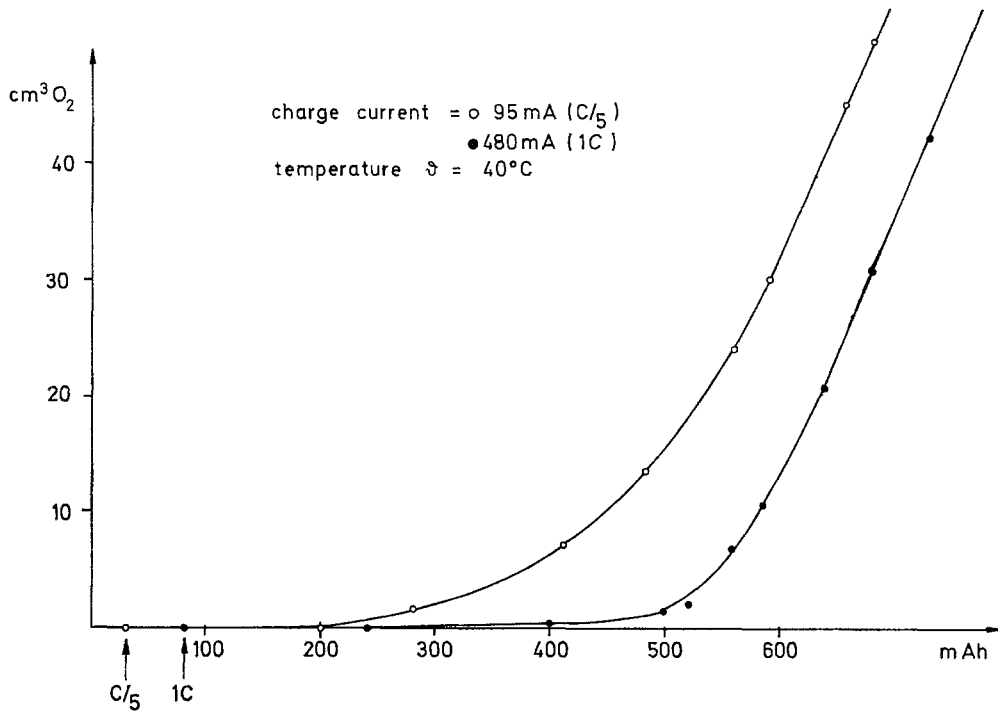Fig. 4. Oxygen evolution at different temperatures.

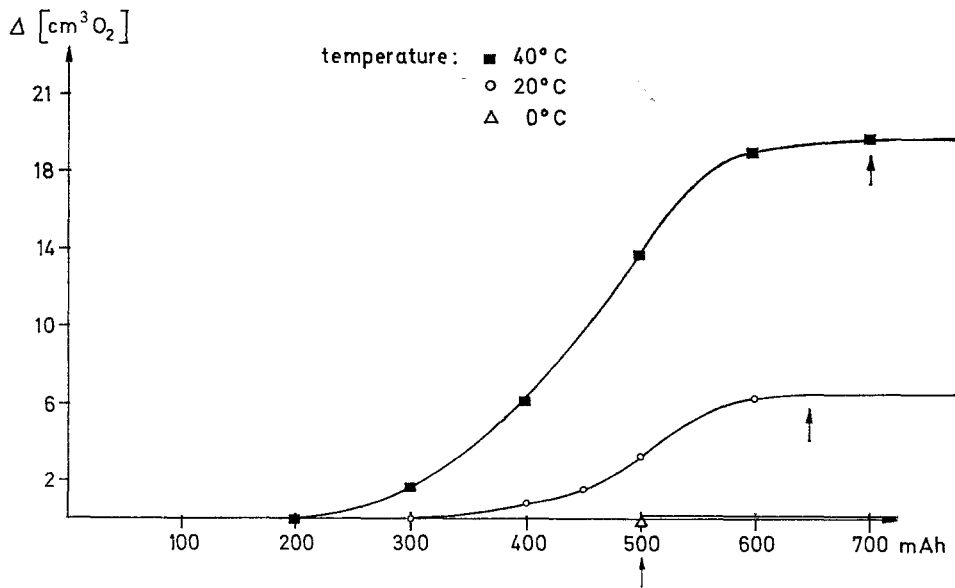Fig. 5. Oxygen evolution v. charge capacity at different charge currents.

Fig. 6. Oxygen volume difference v. capacity at different temperatures.

For $\delta = 40°C$ one obtains, according to (3), a CPC of $L = 2\cdot9 \times 10^{-4}$ A/dm^2 which corresponds to about the 80 h current.

Energy considerations for the most favourable charging conditions

Since the losses due to gassing vary considerably, it is important to know at which electrolyte temperature or current the nickel electrode is charged. A plot of the gas volume difference of the charge currents 1 C and C/5 v. the capacity, is shown in Fig. 6.

For an electrolyte temperature of 40°C, the differences are rather large, since gassing during charging with C/5 begins early. After a short transition period the curve levels off, indicating that both electrodes produce equal amounts of gas. The height of this plateau indicates how much more oxygen is formed when charging with 1 C. With decreasing temperature the differences in the collected gas volumes decrease and therefore the energy-charge current relation is of lesser importance. The explanation for this result may be found in the low self-discharge rate of nickel oxide at low temperatures. At 0°C the rate of the decomposition reaction is so low that its contribution to the gas volume is negligible. However, the water decomposition is dependent only upon a certain state of charge. The difference between the collected gas volumes at currents C/5 and 1 C is therefore close to zero. The magnitude of charge current at 0°C is unimportant. It can also be seen from Fig. 6 (see arrow) that the times at which the volume difference becomes constant, shift to lower values as the temperature decreases. This means that at room temperature the useful discharge capacity is smaller when the charging temperature is kept low. This fact can be explained by a total polarization increase during charging. The experimental results, as shown in the figures, indicate that the most favourable parameter combination of current and temperature during galvanostatic charging of positive nickel sinter electrodes depends upon its later use in practice. If the charge–discharge cycle specifications require a high electrode capacity at minimum energy investment, an electrolyte temperature of 40°C and a charge current of 1 C should be recommended. How far temperature and current can still be increased has yet to be investigated. If, however, in a different case, the electrode is only partially discharged (85% of the total charge) and can accordingly be charged with the equivalent charge, then the most favourable charging conditions are at low electrolyte temperature (for instance 0°C) and any desirable current (C/5 or 1 C) (Fig. 4). The low temperature has the advantage of a slow nickel oxide decomposition whilst no water decomposition is possible due to the electrode potential. It is therefore not possible to give a generalized parameter combination for the charging of positive nickel sinter electrodes for all uses since they depend strongly upon the later practical requirements.

References

[1] H. Bode, K. Dehmelt and J. Witte, *Z. anorg. allgem. Chemie, Bd.* **366** (1969) 1.
[2] B. E. Conway and P. L. Bourgault, *Can. J. chem.,* **37** (1959) 292.