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Optimizing of a Zn/KOH/O_2 cell with silver cathode

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The effect of oxygen overpressure (300–600 mm Hg) of temperature (20–70°C) and electrolyte concentration (2–7 N) upon the performance of a chemical cell of the Zn-oxygen type with silver cathode (gas electrode DSK type) has been studied. The dispersion analysis of data obtained from discharge curves using a variable resistor has been employed in testing the significance of the effect of varying the working parameters. The optimal values of working parameters have been obtained by optimization through a factorial experimental program: 400–500 mm Hg; 67–68°C and 5·9 N.

1. Introduction

Recent studies [1–7] have shown that cells comprising a zinc anode and an oxygen electrode of the porous silver type operating in KOH solution suffer relatively little polarization on discharge [8]. Generally, the efficiency of a chemical cell depends both on the thermodynamic yield of the reaction under working conditions [9] and on the electrical yield of the cell. Its value changes with the extent of irreversible losses (charge transfer, concentration and ohmic polarization). The performance reached depends both on the constructive solution chosen and on the stability of working parameters.

In the present work, the aim has been to establish the optimal value of the working parameters (oxygen overpressure, temperature and electrolyte concentration) for a Zn/KOH/O_2 cell with silver cathode (gas electrode DSK type).

2. Experimental

A chemical cell of the type

$$(-) \quad Zn/KOH/O_2(Ag) \quad (+)$$

with a 99·9% Zn anode and concentrated KOH solution has been developed.

The cathodes were obtained by pressing ($2{\cdot}8 \times 10^8$ N m^{-2}) and sintering in hydrogen atmosphere (15 min at 375°C). The composition of the initial powder mixtures was 81·25% silver carbonate (less than 5 μm) and 18·75% ammonium bicarbonate (40–60 μm). The overall average porosity of the electrodes (as determined by weighing before and after soaking with toluene) was 30·5%.

The cell was discharged through a variable resistor in a wiring scheme which included: an electronic millivoltmeter (Universal Röhrenvoltmeter), type 187a (precision ± 2 mV), a milliammeter type DU 20 (precision ± 1%), a decade resistor box (precision ± 0·1 Ω).

The basic parameters have been varied as follows: oxygen overpressure within 300–600 mm Hg in steps of 100 mm Hg (± 2 mm Hg precision); concentration between 2 and 7 N in steps of 1 mEq cm^{-3} (± 0·005 mEq cm^{-3} precision); temperature between 20 and 70°C in 10° steps (± 0·1°).

2.1. *The effect of changes in working parameters*

E–i discharging curves have been interpreted according to the method advanced by Gilvarry and Slaughter [10]. The values of polarization losses (σ) and average conversion efficiency (η_m), average apparent current density (i_m) and maximum power (P_{max}) have been calculated (these parameters correspond to conditions when maximum power is drawn from the cell). The plots in Fig. 1 show the effects of concentration (a), temperature (b) and oxygen overexposure (c) on the electric characteristics of the Zn/KOH/O_2 source: they indicate a domain of optimal functioning, around the set of values 6 N, 60–70°C, 400–500 mm Hg.

The effect of the electrolyte concentration upon the performance of the chemical source under study is accounted for by the influence of

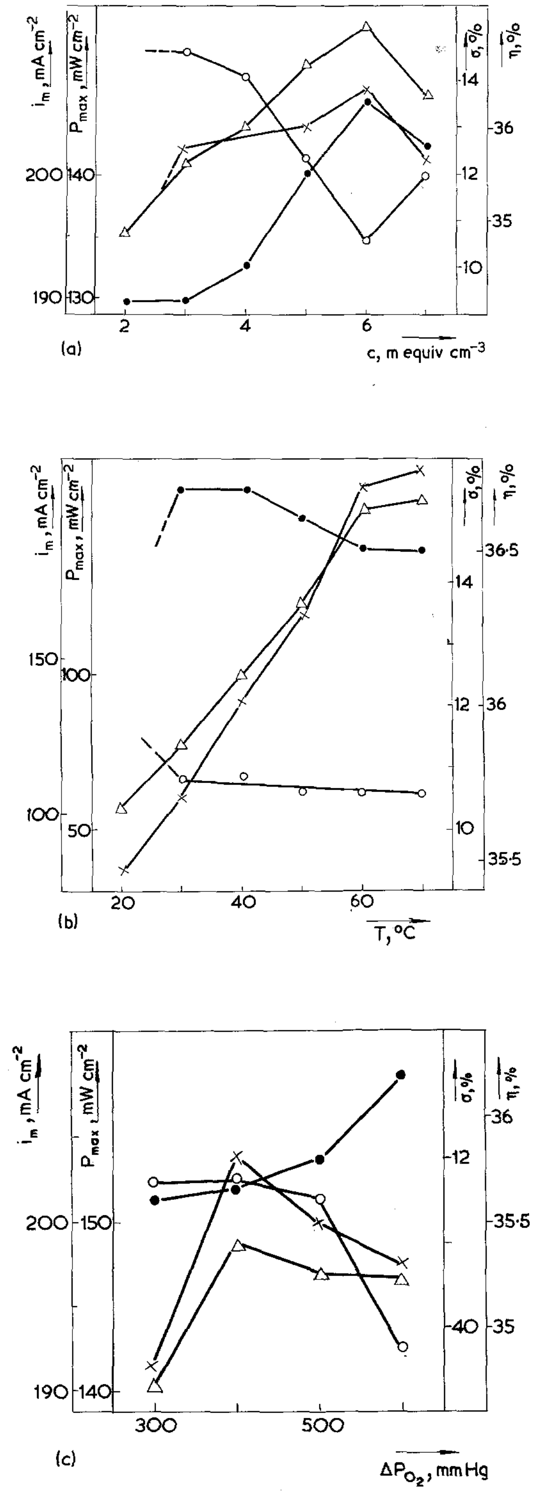

Fig. 1. The effect of concentration (a), temperature (b) and oxygen overpressure (c) on polarization losses σ (o), average conversion efficiency η_m(•), average apparent current density i_m(X) and maximal power P_{max}(△). (a) 60° C, 400 mm Hg; (b) 6 N, 400 mm Hg; (c) 5 N, 60° C.

concentration on the solubility of oxygen, on the anodic dissolution of Zn, and on electrolyte conductivity. It is in good agreement with previous studies on the behaviour of silver gas electrodes in oxygen reduction [7]. Since the anodic dissolution of zinc is practically not affected by concentration change within the studied range (one considers that for pH 12 the solubility of Zn in the KOH medium is a maximum [11]) the effects are due to cathodic processes and electrolyte conductivity changes. The solubility of oxygen in KOH solutions decreases with increasing concentration [12], but this effect is compensated for by the important increase of electrolyte conductivity [13] which has a maximum at a concentration of about 6 N [14]. This behaviour of the Zn-oxygen chemical source coincides with the variation of the apparent activation energy characteristic for the reduction of oxygen in a KOH medium on silver gas electrodes of this type. The latter gives minimum values within the 5–6 N range [15].

The performance improvement of the studied cell as a result of electrolyte temperature increases is explained by its favourable effect on electrolyte conductivity [13] and on the development of anodic and cathodic processes which prevail over the unfavourable effect on oxygen solubility [12]. The electrolyte temperature increases favour anode dissolution, the speeding up of the cathodic reaction and the diffusion of reacting species and reaction products towards (from) the electrodes. The results agree with previous work [15] and data available in the literature [3, 14, 16].

The performance increase of the Zn-oxygen cell following the increase of gas feed overpressure up to 400–500 mm Hg may be explained by its favourable effect upon oxygen solubility and extension of the triphase reaction zone at the cathode. The overpressure increase towards the top limit of the studied range leads to a discharge of oxygen through the largest diameter electrode pores which influence favourably the polarization losses; this is due to electrolyte stirring and to the prevention of anode passivation by zincate layers. The maxima of current density and power corresponding to an overpressure of 400 mm Hg are explained by the triphase reaction zone reaching a maximum for this value of overpressure.

The data discussed above illustrate the complexity of the effects of varying the working parameters and their interdependent character. Establishing optimal values for these parameters requires exploration of the zone: 5–7 N; 50–70°C; 400–500 mm Hg.

2.2. *Dispersional analysis*

The electric characteristics of the Zn-oxygen cell within the optimal working range are calculated. In order to carry out dispersional analysis [17], a three-factor model has been chosen (A = overpressure, B = temperature; C = concentration) with two (400, 500 mm Hg), three (50, 60 and 70°C) and three (5, 6 and 7 N) levels, respectively.

Examination of the results shows that for all electric characteristics (σ, η_m, i_m, P_{max}), the effect of varying factor A (overpressure) and of second order interactions AB (overpressure-temperature) and AC (overpressure-concentration) is not significant. However, the dispersional analysis has evidenced the significance of the effect of concentration (C) variation on polarization losses and average conversion efficiency and of temperature (B), concentration (C) and temperature-concentration interaction (BC) upon average apparent current density and maximal power. The relatively low dispersion induced by random factors (residual dispersion, s_r) indicates a satisfactory accuracy of experimental data and points to the fact that the third order interaction (ABC) is not significant.

The values of the standard deviations of the experimental data are: (1) polarization loss, $\sigma \pm 2{\cdot}4\%$; (2) average conversion efficiency, $\eta_m \pm 1{\cdot}2\%$; (3) average apparent current density, $i_m \pm 8{\cdot}4\ \mathrm{mA\ cm^{-2}}$; (4) maximum power, $P_{max} \pm 7{\cdot}7\ \mathrm{mW\ cm^{-2}}$.

2.3. *Optimization*

According to the data presented above, the dispersional analysis has allowed the separation of parameters whose effect is significant (concentration and temperature) with a view to carrying out the optimization study of the chemical cells under study.

One considers the functions which describe the relations between significant independent variables – temperature (x_1) and concentration (x_2) – and dependent variables (y) – polarization loss, conversion efficiency, apparent current density and power are as follows:

$$y = b_0 + b_1x_1 + b_2x_2 + b_{12}x_1x_2 + b_{11}x_1^2 + b_{22}x_2^2.$$

The calculation of the coefficients of the regression functions ($b_0 \ldots b_{22}$) for each dependent variable has been effected [17] starting with data obtained from a program of factorial experiments (an orthogonal system of $3^2 = 9$ experiments symmetrical with a central point whose coordinates are 60°C; 6 N). It was considered that units of 10°C and 1 m Eq $\mathrm{cm^{-3}}$, respectively, are characteristic of the variations of working parameters. The coded values of independent variables correspond to:

$$-1 = 50°\mathrm{C}; 0 = 60°\mathrm{C}; 1 = 70°\mathrm{C} \quad (\text{for } x_1);$$

$$-1 = 5\,\mathrm{N}; 0 = 6\,\mathrm{N}; 1 = 7\,\mathrm{N} \quad (\text{for } x_2).$$

To check up on the validity of the regression functions, y_{calc} of each electric parameter has been calculated for each concentration-temperature set and the deviation of values observed from those calculated has been verified (the linearity of regression functions has been verified).

By equating to zero the partial derivatives of the regression functions with respect to the two independent variables, a system of two linear equations has been obtained for each electric characteristic; solving them has led to the establishment of optimal values of independent variables whose performances are maximum.

Examination of results shows that for all electric characteristics under study, the calculated F's are lower than critical F_α's corresponding to a significance limit $\alpha = 0{\cdot}01$. Thus one can accept the zero hypothesis and draw the conclusion that the regression functions established describe satisfactorily the relations between variables within the optimal working range.

The regression functions have been employed in plotting the response curves in the plane of the two significant parameters for polarization losses, average conversion efficiency, apparent current density and maximal power (Fig. 2).

Examination of the curves in Fig. 2 shows that the centres of response curves P_{max} and i_m are close to each other (5·99 N – 66·5°C and, 5·92 N – 68·5°C respectively). The shift of the maximum between these two points is not significant (for the coordinates of P_{max}, $i_m > 200\ \mathrm{mA\ cm^{-2}}$ and since the reliability interval for apparent current density is $\pm 8{\cdot}4\ \mathrm{mA\ cm^{-2}}$; this is not insignificant). The centre of the response curves η_m is shifted toward lower temperatures; the shift is significant since its coordinates correspond to an average apparent

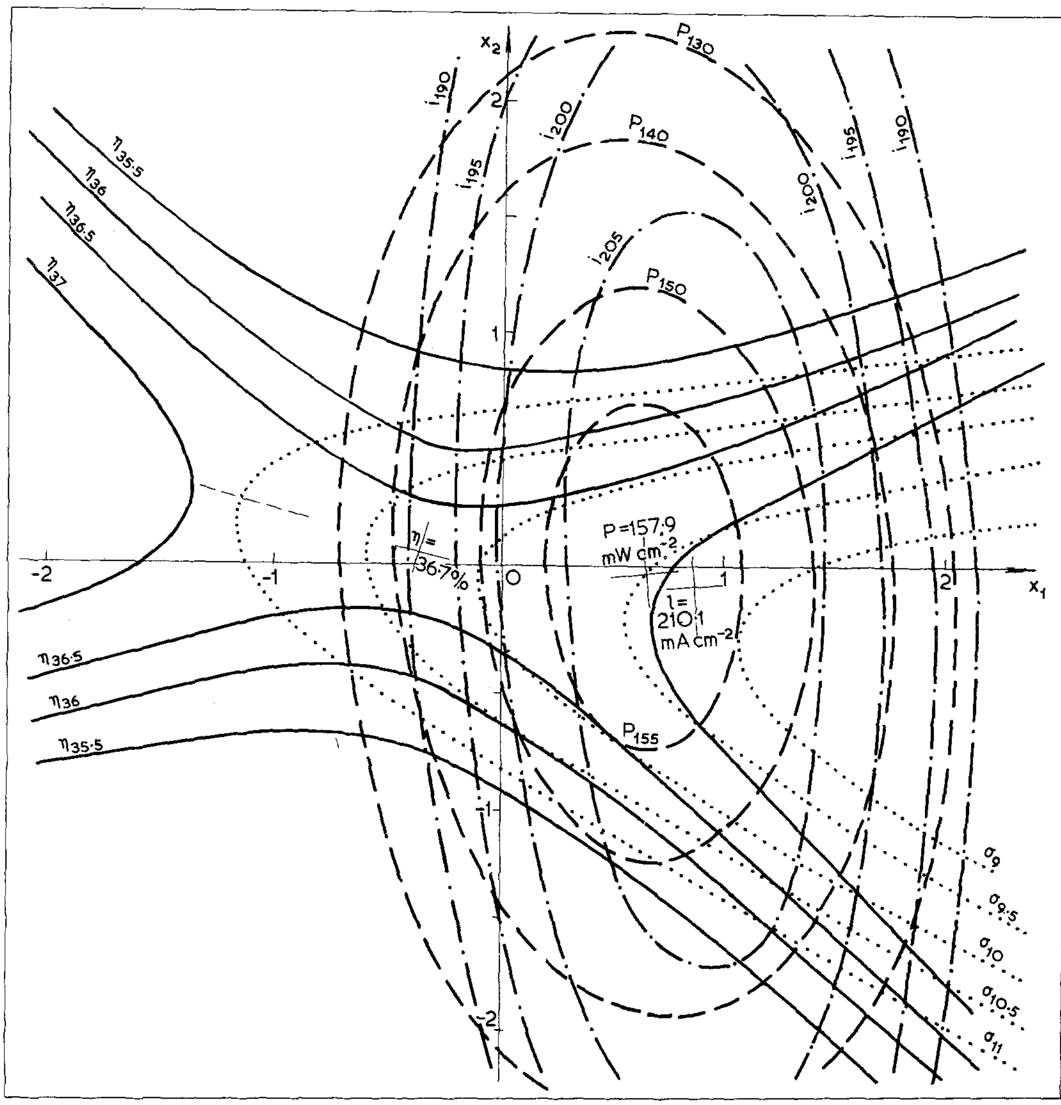

Fig. 2. Response curves in the plane of the two parameters with significant effect (ΔP_{O_2} = 400–500 mm Hg). . . . σ; —— η_m; — · — · — i_m; — — — P_{max}.

current density i_m < 195 mA cm^{-2}. The centre of the response curves σ is shifted toward much higher temperatures. This range does not present any practical interest due to the outstanding difficulties one comes across during operation (increase of vapour pressure of the electrolyte, high heat losses, strong corrosion of the KOH medium, the increase of weight and decrease of specific power, etc.). Values between 9 and 9·5% for polarization losses corresponding to coordinates of centres of response curves i_m and P_{max} may be considered reasonably low. For the coordinates, maximum power and average apparent current density, the value of average conversion efficiency is higher than 36·5%, which is close to the maximum one (36·7%), the difference being insignificant (lower than the standard deviation ± 1·2%).

These data allow the establishment of the optimal working parameters of the cell for the overpressure range 400–500 mm Hg: KOH concentration 5·9 N, temperature 67–68°C. In these conditions the cell offers an average conversion efficiency of 36·5% with polarization losses of 9·5%; the average apparent current density is 210 mA cm^{-2} while power is 157 mW cm^{-2} under conditions of maximum power draws by the external circuit.

3. Conclusions

The study of the effect of changes in working parameters upon the performance of a chemical source of the Zn/KOH/O_2 type with silver cathode (gas electrode DSK type) has revealed the favourable effects of a concentration increase up to 6 N, of temperature at the limit of the studied range (70°C) and of feed gas overpressure up to 400–500 mm Hg. The dispersional analysis of experimental data has revealed the insignificant effect of overpressure change within the range 400–500 mm Hg. The optimization calculation has led to the establishment of optimal conditions of concentration and temperature (for ΔP_{O_2} 400–500 mm Hg, about 5·9 N and 67–68°C, respectively) which ensure the maximum performance of the cell: polarization losses lower than 9·5%, average conversion efficiency higher than 36·5%, apparent current density 210 mA cm^{-2} when a maximum power of 157 mW cm^{-2} is drawn from the cell.

Acknowledgements

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