JOURNAL OF APPLIED ELECTROCHEMISTRY 6 (1976) 135–138

Activated nickel anodes for average power fuel cells

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Received 5 February 1975

The activation of nickel gas anodes has been studied using a wide range of transition metal compounds added to the nickel powder before sintering or added by impregnation to the sintered electrodes. Using a hydrogen-oxygen fuel cell for the tests, the efficiency of the impregnant for increasing the performance of the nickel/hydrogen electrode was in the range ammonium wolframate > cobalt acetate > copper basic carbonate > ammonium vanadate. The optimum performance was obtained by using a mixture of the first two compounds. The optimum conditions for the use of these electrodes are shown to be 79–82°C with a KOH electrolyte of 6·5–6·7 N and a hydrogen pressure at the electrode of 400 mm Hg. Under these conditions the cell gave 300 mA cm^{-2} and a maximum power density of 110 mW cm^{-2}.

1. Introduction

There are two alternatives one can consider in order to improve the performance of gas electrodes: (1) achieving a suitable microgeometrical structure and (2) improving local intrinsic activity of the surface by using electrocatalysts. The conditions of preparing DSK (double skeleton) type nickel gas electrodes, with a suitable microgeometrical structure, have been reported in a previous paper [1].

In this work, the effect of the activation of nickel gas electrodes with different electrocatalysts has been studied. Various considerations have led us to choose, as electrocatalysts, transitional metals with an average overpotential and a relatively weak metal-hydrogen bond [2–5]. Then, in the case of the best electrode which was found among those studied in the present paper (i.e. the nickel gas anode activated with ammonium wolframate and cobalt acetate), the optimum working parameters have been established.

2. Experimental

2.1. *Preparation of the electrodes*

The optimum conditions for preparation of DSK type nickel gas electrodes, from an initial powder mixture containing 25% carbonyl nickel, 50% nickel carbonate, and 25% oxalic acid are: compression at $4{\cdot}6 \cdot 10^8$ N m^{-2} and sintering in a hydrogen atmosphere at 700°C for 30 min [1]. We shall refer to the electrodes obtained this way as 'standard electrodes', designated *m* in Tables 1 and 2.

Electrode activation was carried out by two methods:

First method. The active catalytic compound and the other powders were blended before compressing and sintering.

By this method nickel gas electrodes were prepared from (a) a powder mixture of 15% carbonyl nickel, 50% nickel carbonate, 25% oxalic acid, and 10% of various activation compounds (TiO_2, MnO_2, ZrO_2, V_2O_5, Cr_2O_3, $(NH_4)_2WO_4$, $Co(CH_3COO)_2$, $(NH_4)_2WO_4 + Co(CH_3COO)_2$, NH_4VO_3). These electrodes were termed A1..A9. (b) a powder mixture of 25% carbonyl nickel, 40% nickel carbonate, 25% oxalic acid, and 10% of various activation compounds ($2CuCO_3 \cdot Cu(OH)_2$, $(NH_4)_2WO_4$, $Co(CH_3COO)_2$, NH_4VO_3, TiO_2, MnO_2, ZrO_2, V_2O_5, Cr_2O_3). These electrodes were called B1..B9.

Second method. The standard electrodes were impregnated with a suitable salt solution of the electrocatalytic metal (0·3 M NH_4VO_3, 1 M $Co(CH_3COO)_2$, 0·3 M $2CuCO_3 \cdot Cu(OH)_2$). These electrodes are referred to as C1..C3. After impregnation, the electrodes were heated to 400°C in a hydrogen atmosphere for 1 h.

Microscopic examination of these electrodes was carried out by a IOR MC-1 type metallographic microscope (500 x). The total porosity was determined by weighing the electrodes before and after impregnation with toluene.

2.2. *Electrochemical measurements*

The efficiency of activation of the nickel electrodes was studied by comparing performances in the following hydrogen-oxygen fuel cells:

$$(-)\,(Ni)\,H_2/KOH/O_2\,(Ag)\,(+)$$

where the electrodes were a nickel, or activated nickel, gas anode and a previously studied [6] silver gas cathode, of 30·5% porosity.

The fuel cell operating conditions were: room temperature, 6 N KOH concentration, 400 mm Hg hydrogen/oxygen overpressure.

The *E* versus *i* curves were plotted on discharging the cells through a variable resistor in a wiring scheme [7], which included a Radiometer 22 type electronic millivoltmeter (precision ±1 mV), a DU 20 type milliampermeter (precision ±1%), and a decade resistor box (precision ±0·1 Ω).

Finally, in order to establish the optimum working range for the fuel cell with a nickel anode activated by $(NH_4)_2WO_4$ + $Co(CH_3COO)_2$, the working parameters have been varied as follows: hydrogen over pressure at 400 and 500 mm Hg, electrolyte concentration at 5, 6 and 7 N, and temperature at 60, 70 and 80°C.

3. Results

Electrical performances of the hydrogen-oxygen fuel cells with nickel or activated nickel anodes and silver cathodes, calculated from *E* versus *i* discharging curves by a method previously described [7] are listed in Table 1. The electrical performances of the hydrogen-oxygen fuel cell with nickel gas anode activated by $(NH_4)_2WO_4$ + $Co(CH_3COO)_2$ and silver gas cathode in different working conditions are given in Table 2.

4. Discussion

4.1. *The efficiency of the electrocatalytic active substances*

Activation of nickel gas electrodes with transitional metal oxides (Ti, Mn, Zr, V, Cr)–A1..A5, and B5..B9 electrodes–is not convenient for it diminishes too much the mechanical strength of the electrodes.

The mechanical strength of the A6, A7 and A9 electrodes was much lower than that of the B2, B3 and B4 electrodes, irrespective of the content in electrocatalytic compound. In the case of the A electrodes it was 10% of the carbonyl nickel which was removed by substituting the electrocatalytic compound, while for the B electrodes the electrocatalytic compound replaced 10% of the initial nickel carbonate. Consequently, the final content

Table 1. Electrical performances of the fuel cells with nickel or nickel activated anodes ($\Delta P_{H_2} = 400$ mm Hg, $\Delta P_{O_2} = 400$ mm Hg, KOH 6 N, 25°C)

Anode	*Average electrical voltage* $E_m = E_r - i_m R$ (mV)	*Average apparent current density* $i_m = \frac{1}{2} E_i^2 / E_t R$ (mA cm^{-2})	*Maximum apparent power density* $P_{max} = i_m^2 R$ (mW cm^{-2})	*Average conversion efficiency* $\eta_m = (E_i - E_r)/2E_t$ (%)
M	367·5	68·7	25·2	29·87
A8	335·0	95·7	32·0	27·23
B1	503·0	76·3	33·7	35·96
B2	460·0	88·4	40·7	37·40
B3	447·5	84·4	37·7	36·58
B4	372·5	70·3	26·2	30·28
C1	375·0	63·5	23·8	30·49
C2	467·5	69·8	32·6	38·00
C3	410·0	64·0	26·2	33·33

* The A1..A7, A9 and B5..B9 electrodes did not have a suitable mechanical strength for their electrochemical study.

Table 2. The performances of the fuel cell with A8 anode in different working conditions

Working conditions *Temperature* (°C)	 *Concentration* (N)	 ΔP_{H_2} (mm Hg)	*Average apparent current density* (mA cm^2)	*Maximum apparent power density* (mW cm^2)	*Average conversion efficiency* (%)
60	5	400	143·7	49·6	28·75
		500	141·9	49·3	28·95
	6	400	157·0	53·0	28·12
		500	150·0	49·5	27·50
	7	400	162·8	57·0	29·17
		500	156·5	56·3	30·00
70	5	400	259·3	90·7	29·41
		500	282·5	98·2	29·20
	6	400	275·0	98·3	30·04
		500	273·1	96·9	29·83
	7	400	264·8	94·7	30·04
		500	246·5	88·1	30·04
80	5	400	294·0	108·0	31·14
		500	280·7	102·5	30·93
	6	400	306·0	117·0	32·41
		500	300·0	112·5	31·78
	7	400	308·4	114·1	31·36
		500	312·5	117·2	31·78

in carbonyl nickel was 15% for the A electrodes and 25% for the B electrodes. As carbonyl nickel gives the resistant body of the electrodes, the friability of the A electrodes is easily understood.

The purpose of this work is to establish the effect of the nickel gas anode activation in order to achieve gas electrodes suitable for average power sources. All the electrical characteristics (E_m, i_m, P_{max}, η_m) are given in Table 1, but for average power sources, the most important electrical characteristic is the current density at a given voltage. Consequently, the effect of activation is discussed with respect to the current density.

Comparative examination of data listed in Table 1 shows that at a given cell voltage:

(i) The activation of nickel gas electrodes with transitional metals does increase the average apparent current density;

(ii) The *first method* of activation leads to much better results than the *second method*;

(iii) As seen in Table 1, the efficiency of the electrocatalytic-active substance decreases as follows: ammonium wolframate (B2) > cobalt acetate (B3) > copper basic carbonate (B1) > ammonium vanadate (B4). The highest average apparent current densities are: 88·4 mA cm^{-2} (B2) and 84·4 mA cm^{-2} (B3); these are about 25% greater than that of the unactivated nickel electrode (M) – 68·7 mA cm^{-2}.

4.2. *The optimum working parameters for a hydrogen-oxygen fuel cell with an activated nickel anode*

In order to establish the optimum KOH concentration and temperature for the hydrogen-oxygen fuel cell, a chemical source with activated nickel anode and silver cathode has been studied. The anode was the A8 electrode activated with a mixture of the best electrocatalysts (ammonium wolframate and cobalt acetate). This electrode had the highest current density, about 30% greater than the unactivated electrode.

From preliminary studies which are not reported here we have found that the optimum KOH concentration and temperature are approximately 6–7 N and 70°C; this is also in good agreement with literature data [8, 9]. Here, a three factors mathematical model is used for carefully investigating this region (see Table 2) by dispersional analysis [10]. The three factors are: A = hydrogen overpressure, B = temperature, C = electrolyte concentration, with, respectively, two (400 and 500 mm Hg), three (60, 70 and 80°C), and three (5, 6 and 7 N) levels. By dispersional analysis (Fischer's test) we found that the effect of variation of the A factor and of the second order interactions AB and AC is not significant.

One considers that the functions which describe the relations between the significant independent variables, i.e. temperature (x_1) and concentration (x_2), and the dependent variables, i.e. apparent current density (y_1), maximum power (y_2) and conversion efficiency (y_3), are as follows [10]:

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

The calculation of the regression function coefficients ($b_0..b_{22}$) for each dependent variable has been done starting up with data obtained from a program of factorial experiments, symmetrically distributed against a central point whose coordinates are 70°C, 6 N. The coded values of independent variables correspond to:

$$-1 = 60^\circ\text{C};\ 0 = 70^\circ\text{C};\ 1 = 80^\circ\text{C}\ (\text{for } x_1)$$

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

The regression functions for the electric characteristics are:

$$y_1 = 270{\cdot}6 + 74{\cdot}15x_1 + 4{\cdot}1x_2 + 1{\cdot}6x_1x_2 - 40{\cdot}7x_1^2 - 5{\cdot}7x_2^2$$

$$y_2 = 96{\cdot}17 + 29{\cdot}7x_1 + 2{\cdot}4x_2 + 0{\cdot}825x_1x_2 - 12{\cdot}3x_1^2 - 2{\cdot}4x_2^2$$

$$y_3 = 29{\cdot}6 + 1{\cdot}4x_1 + 0{\cdot}67x_2 - 0{\cdot}02x_1x_2 + 0{\cdot}433x_1^2 + 0{\cdot}133x_2^2.$$

By equating to zero the partial derivatives of regression functions, the apparent current density maximum is obtained at 6·5 N and 79°C, while the power density maximum shows up at 6·7 N and 82°C. The difference between the values of i_m and P_{max} in the points 6·5 N – 79°C (306·8 mA cm^{-2}, 113·9 mW cm^{-2}) and 6·7 N–82°C (301·7 mA cm^{-2}, 115·2 mW cm^{-2}) is lower than the reliability interval (± 14·6 mA cm^{-2}, ± 6·1 mW cm^{-2}). Under these optimum conditions, the cell has an average conversion efficiency of 31·5%.

Of course, as can be seen from Table 2, the optimum range has been approached only from the region of lower temperatures. Obviously, this is very satisfactory indeed for practical purposes, taking into account the severe corrosion, thermal losses and other unfavourable effects which become very limiting at higher temperatures.

5. Conclusions

The efficiency of electrocatlytic active substances added for the improvement of nickel gas electrode performances decreases as follows: ammonium wolframate > cobalt acetate > copper basic carbonate > ammonium vanadate.

The optimum values of working parameters for the hydrogen-oxygen fuel cell with a nickel gas anode activated by ammonium wolframate and cobalt acetate – and with a silver gas cathode are: 6·5–6·7 N KOH concentration, 79–82°C temperature. In these conditions, the cell under study offers an apparent current density of 300 mA cm^{-2} and a power density of 110 mW cm^{-2}. Besides, there is an interesting conclusion about the shape of the curve current density versus temperature at constant concentration. So, at 6·5 N KOH, there is only a 10% increase in the average current density as temperature goes up from 70 to 80°C, but there is a spectacular decrease of 45% in the average current density as temperature goes down from 70 to 60°C. Consequently, the cell should be stabilized provided that temperature be kept in the range of approximately 70–80°C.

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