JOURNAL OF APPLIED ELECTROCHEMISTRY **21** (1991) 313–316

Gas-diffusion electrodes catalysed with tungsten carbide as anodes for nickel electrowinning

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Received 30 March 1990; revised 10 July 1990

The characteristics of gas-diffusion electrodes catalysed with tungsten carbide have been investigated under the conditions of nickel electrowinning. It is shown that their use as anodes in this process leads to a considerable decrease of the energy consumption and the nickel produced is free of heavy metal impurities.

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1. Introduction

Nickel is gaining considerable importance in connection with some fast developing fields such as spacecraft engineering, aviation, electronics, etc. For these applications the purity of nickel is of primary significance. One of the principal methods for production of nickel with high purity is electrowinning.

The electrolytic baths used for this purpose comprise nickel stationary or rotating cathodes and lead, graphite or soluble nickel anodes. The disadvantages of these baths are the high voltages required for their operation and the contamination of the obtained nickel with lead, iron, cobalt, copper or sulphur, as a result of which its purity cannot exceed 99.94% [1].

In a previous paper we have shown a possible method for obtaining a significant decrease of the electrical energy consumption in zinc electrowinning by replacing the lead-silver anodes with hydrogen tungsten carbide gas-diffusion electrodes (GDE) [2]. Moreover, since tungsten carbide is known as a catalyst with high corrosion resistance in acid medium [3], it can be expected that an electrolysis using tungsten carbide GDE would ensure the production of pure metal.

The aim of the present investigation is to study the feasibility of using hydrogen GDEs catalysed with tungsten carbide for the production of pure electrolytic nickel at low energy consumption.

2. Experimental

The performance of hydrogen GDEs was investigated galvanostatically in a cell with a nickel plate as a cathode and a water jacket for temperature control (Fig. 1). A Hg-Hg_2SO_4 electrode was used as reference. The measurements were performed in an electrolyte containing $70\,g\,dm^{-3}$ nickel ions (as sulphate), $10\,g\,dm^{-3}$ sodium ions (as sulphate) and $2.5\,g\,dm^{-3}$ saccharine at 70° C. The electrolyte pH was about 4. Lower pH values were obtained by small additions of sulphuric acid. The current efficiency of nickel deposition was determined by weight gain of the cathode after 4 h electrolysis. During this measurement the respective pH values were corrected at 15 min intervals.

The galvanostatic current-voltage curves were traced with a RADELKIS OH 405 (Budapest) potentiostat with a built-in resistance so that it could be used as a galvanostat. The long term tests were carried out with a custom-built galvanostat (0.5 A, 5 V) designed in the laboratory.

The investigated hydrogen tungsten carbide GDEs were double-layered, consisting of a gas-supplying layer developed by Iliev *et al.* [4] and an active layer containing tungsten carbide and Teflonized carbon black [5]. The working surface area of each electrode was 10 cm.

The carbides used for the catalysis of the double-layered electrodes had a surface area of $6.4\,m^2\,g^{-1}$. It has been shown in our previous studies that carbides with this surface area have lower catalytic activity than those with surface areas of $10–22\,m^2\,g^{-1}$, but they display higher corrosion resistance [3, 6].

The presence of tungsten in the electrolyte was controlled by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a JY38 spectrometer. The purity of the electrolytically deposited nickel was monitored by a JEOL 100 B electron microprobe.

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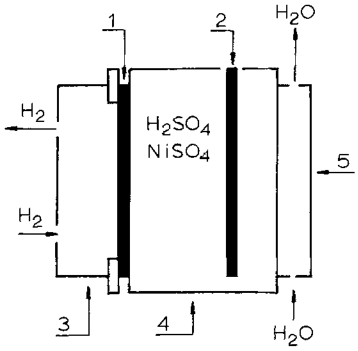

Fig. 1. Diagram of the cell for hydrogen tungsten carbide GDE tests: (1) tungsten carbide gas-diffusion anode; (2) nickel cathode; (3) gas chamber; (4) electrolyte chamber; (5) water jacket for temperature control.

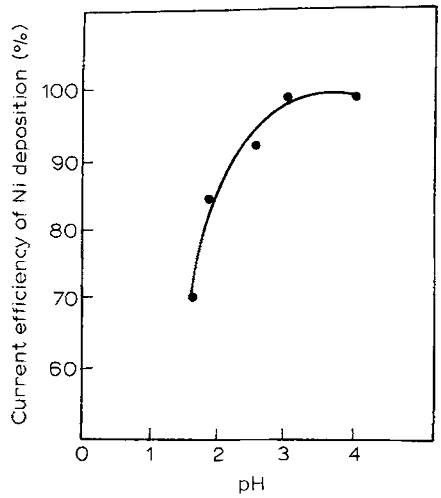

Fig. 3. Influence of pH of the electrolyte on the current efficiency. Electrolyte composition: 70 g dm^{-3} Ni^{2+}, 10 g dm^{-3} Na^+, 2.5 g dm^{-3} saccharine, and small amounts of sulphuric acid for respective pH corrections; temperature 70° C; i = 40 mA cm^{-2}.

3. Results

It was first necessary to check whether the presence of nickel ions in the solution leads to a significant decrease of the catalytic activity of tungsten carbide. For this purpose current-voltage measurements of the tungsten carbide GDEs were performed in sulphuric acid solution and in electrolyte containing $NiSO_4$. As can be seen from Fig. 2, the addition of nickel ions does not affect the polarization of GDEs catalysed with tungsten carbide.

On the basis of this electrode performance it can be estimated that the voltage of the nickel electrowinning cell containing a hydrogen tungsten carbide anode is about 1 V lower than that of a cell with a lead or nickel anode.

It is known from the literature that there is a strong dependence of the current efficiency of nickel deposition on the electrolyte pH [7]. Fig. 3 presents this dependence measured in the cell shown in Fig. 1, containing the electrolyte described in the experimental part. It can be seen that the nickel deposition proceeds with the highest efficiency at pH values of 3–4.

The results obtained posed the following two questions: (a) How much will the tungsten carbide GDE performance deteriorate at these pH values; and (b) what will the corrosion resistance of tungsten carbide be at these pH values.

To elucidate these questions current-voltage measurements and long term tests of hydrogen tungsten carbide GDEs were carried out at electrolyte pH values ranging from 2 to 4.

Figure 4 presents the current-voltage curves taken at pH values of 2 and 4. A comparison with Fig. 2 shows that at i = 40 mA cm^{-2} (the current density of a conventional nickel electrowinning cell) the electrode polarization rises by 100 and 200 mV, respectively. Evidently this will not have marked influence on the cell voltage which remains considerably lower than that of conventional cells with lead-silver (Tainton) anodes (Table 1).

During the long term tests, however, difficulties arose with the maintenance of the pH of the electrolyte. During the hydrogen ionization at the gas-diffusion anode (GDA) the hydrogen ion concentration

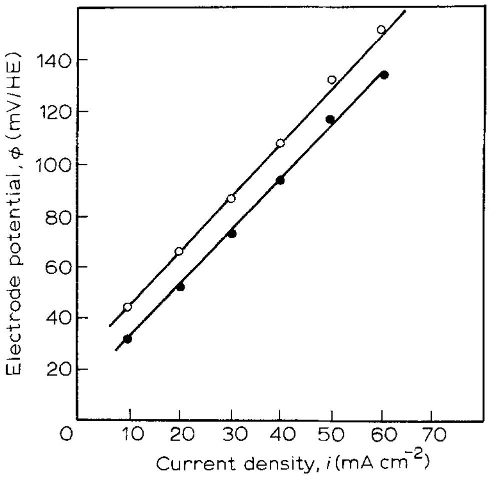

Fig. 2. Current-voltage curves for a tungsten carbide GDE. Active layer composition: 400 mg cm^{-2} WC, 47 mg cm^{-2} Teflonized carbon black. (●) 2.25 M H_2SO_4; (○) 2.25 M H_2SO_4, 10 g dm^{-3} Ni^{2+}; temperature 70° C.

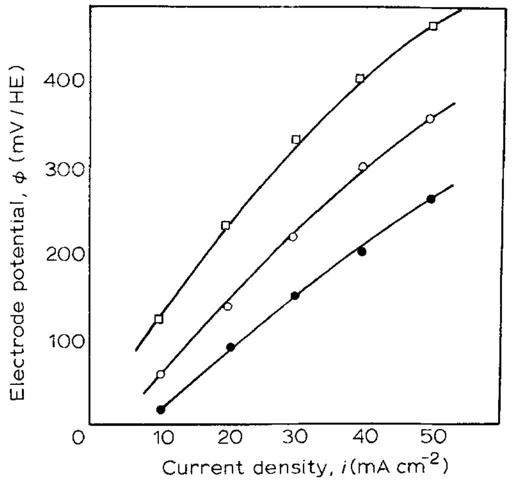

Fig. 4. Current-voltage curves for a tungsten carbide GDE in electrolyte containing: (○) 70 g dm^{-3} Ni^{2+}, 10 g dm^{-3} Na^+, 2.5 g dm^{-3} saccharine, pH = 4; (●) 70 g dm^{-2} Ni^{2+}, 10 g dm^{-3} Na^+, 2.5 g dm^{-3} saccharine 0.5 g dm^{-3} H_2SO_4, pH = 2; (□), pH = 4 after 2000 h operation; temperature 70° C.

Table 1. Anode potentials and cell voltage for nickel electrowinning at $i = 40\,mA\,cm^{-2}$, $t = 70°C$

WC gas-diffusion anode		*Tainton anode*	
$U_{(cell)}$ (V)	$U_{(WC/H_2)}$ (V against HE)	$U_{(cell)}$ (V)	$U_{(Tainton/02)}$ (V against HE)
1.6–1.65	0.250–0.300	2.85	1.71

Table 2. Analytical results for a nickel deposit obtained in a cell with tungsten carbide GDA after 2000 h operation

Element	*Dark area*		*Main bright area*	
	Weight (%)	*Normalized* (*at* %)	*Weight* (%)	*Normalized* (*at* %)
Si	1.23	2.46	–	–
S	1.89	3.31	–	–
Cl	1.70	2.69	–	–
K	1.35	1.93	–	–
Ni	93.83	89.62	100	100

in the electrolyte increased and the pH decreased sharply. Attempts to compensate for these changes by adding nickel carbonate suspension can solve the problem partially. It was found that in the case of small electrolytic cells with a ratio of 1 : 25 between the volumes of the cell and the electrolyte tank and an electrolyte cycling rate of 8–10 $dm^{-3}\,h^{-1}$ the pH can be maintained in the range 3.5–3.0 for 8 h without any corrections. To restore the initial pH value it is necessary to add 20 cm^3 of 10% suspension of nickel carbonate per litre of electrolyte in the cell.

Under these experimental conditions a cell containing a hydrogen GDA was subjected to long term tests of 2000 h. The subsequent X-ray analysis showed the presence of tungsten oxides (WO_2, W_4O_{11} and WO_3) on the electrode surface. Their amount constitutes about 10% of the total carbide content in the electrode.

As seen from Fig. 4 this leads to some 100 mV increase in the polarization, which does not severely affect the energy consumption during the process. Moreover, it can be seen from the Pourbaix diagram for tungsten [8] that, at pH < 4 and anodic potentials of 300–400 mV, the tungsten oxides are stable. It is possible, however, that by adding nickel carbonate for pH correction the electrolyte in the pores of the hydrogen GDA may be alkalized. This possibility together with the steady state potential shift in the anodic direction at open circuit, in the absence of hydrogen, may cause local dissolution of part of the oxides.

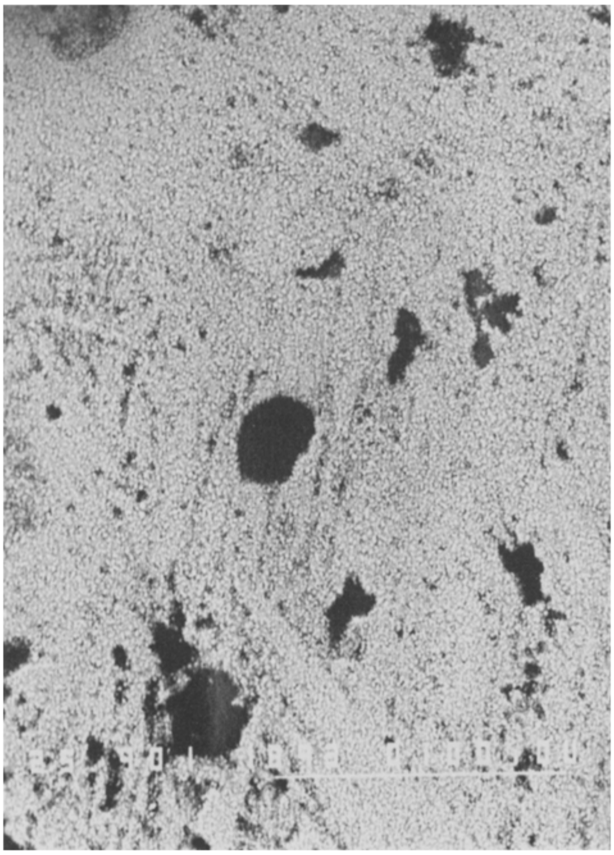

Fig. 5. SEM photograph of nickel deposited in the cell with tungsten carbide anode after 2000 h operation. (× 1000).

Analysis of electrolyte samples after 100 and 2000 h operation showed that the tungsten content in the electrolyte was 1×10^{-3} and 1.64×10^{-3} wt %, respectively. This proves the assumption that under these conditions partial dissolution of the tungsten oxides formed at the anode actually occurs. It remains an open question whether this affects the purity of the electrolytically deposited nickel.

Studies on the purity of nickel deposited after 2000 h of cell operation were performed. The nickel deposits were stripped from the cathode and a polished cross-section was investigated using a JEOL 100B electron microprobe. The SEM photographs (Fig. 5) show the existence of different areas on the nickel surface. The analysis indicates that the purity of the sample is 99.98%. The main bright areas contain nickel with 100% purity, while in the dark areas the purity is 90–94%, the impurities being chlorine, sulphur, silicon and potassium (Table 2). The sample does not contain tungsten or other heavy metals.

The contamination with sulphur has most likely been caused by the sulphate ions in the electrolyte, while the silicon, chlorine and potassium impurities have probably occurred during the specimen preparation.

The good results obtained from the experimental cell initiated further investigations using GDAs with larger surface areas. The performance of these anodes was tested in a pilot installation for production of nickel pellets based on the method developed by Hein and co-workers [9].

The electrolytic cell of the installation was a plastic drum of 80 cm diameter, operated by an electric motor rotating at 30 rpm. Nickel granules with 3–4 mm diameter were used for the cathode which was in the bottom part of the drum. The electrical contact was made by collector fingers. The tungsten carbide GDA ($S = 40\,cm^2$) was mounted on a triangular gas

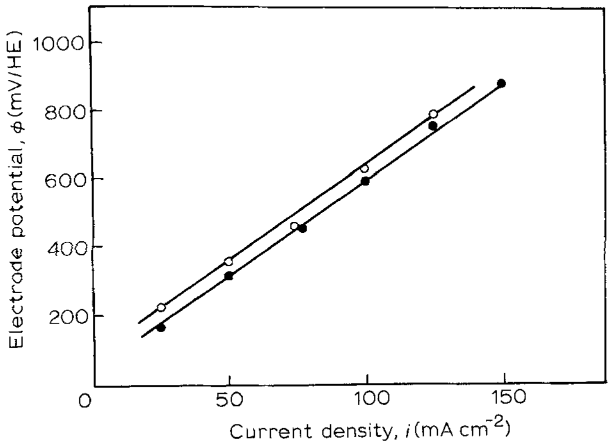

Fig. 6. Current-voltage curves for tungsten carbide GDE obtained in the cell for production of nickel pellets. Electrolyte composition: $70\,g\,dm^{-3}\,Ni^{2+}$, $10\,g\,dm^{-3}\,Na^{+}$, $2.5\,g\,dm^{-3}$ saccharine; temperature 40° C. (○) After 4 h operation; (●) after 6 h operation.

chamber of stainless steel, fixed statically on a rolling axis. Unpolarized nickel wire fitted adjacent to the anode was used as reference electrode. The electrolyte composition was as given earlier. The electrolysis proceeded at 40° C.

Figure 6 shows the current-voltage characteristics of the tungsten carbide GDA obtained after 4 and 6 h operation of the cell. The slightly higher polarization in comparison with that obtained by using anodes with a surface area of $10\,cm^2$ (Fig. 4) can be attributed to the lower temperature of this experiment. The voltage needed for the electrowinning process in the installation with GDA is 5.5 V, while the use of lead-silver (Tainton) anodes requires a voltage of 7 V [9]. The remarkably higher voltage necessary for the electrolysis in these cases is due to the greater ohmic losses in the electrolytic cell. After 8 h of electrowinning at $i = 50\,mA\,cm^{-2}$ and pH $\sim$ 3 the diameter of the nickel pellets reached 10 mm. The nickel obtained was of dull colour and free of lead because of the tungsten carbide GDA used.

It can be concluded from the results that the use of hydrogen tungsten carbide GDEs as anodes for nickel electrowinning leads to a decrease of the cell voltage (and energy consumption) by some 30% and to the production of nickel free of heavy metals.

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