

Short Communication

Ruthenium-based, inert oxide electrodes for impregnating active materials in nickel plaques

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Abstract

Titanium electrodes coated with mixed ruthenium–iridium–titanium oxides are tested as inert counter electrodes for impregnating active materials in porous nickel plaques. The latter are to be used as the positive electrodes in nickel/cadmium cells. Weight losses and variations in bath voltage have been monitored while using these electrodes in the impregnation bath. A 2.85 Ah nickel/cadmium cell has been constructed using nickel electrodes developed by employing the coated electrodes of this study. The performances of these coated electrodes are compared with those of platinum electrodes that are currently employed by nickel/cadmium battery manufacturers. The results are found to be satisfactory.

Keywords: Electrodes; Nickel plaque; Nickel/cadmium batteries; Electrochemical impregnation; Nickel/cadmium cells; Ruthenium

1. Introduction

During the development of positive electrodes for nickel/cadmium cells, active materials are deposited into the pores of the positive plaques either by chemical or by electrochemical impregnation techniques [1]. In the electrochemical impregnation (EI) method, the active material is cathodically deposited from a nickel nitrate bath.

The negative electrodes that are generally used in EI baths are nickel sheets [2], platinum-coated titanium sheets [3], and platinum or platinum meshes/exmets [3]. These electrodes are expensive and suffer dissolution during electrolysis. The latter effects the structural integrity of the electrodes. Hence, it is desirable that an alternate inexpensive and stable material is developed for the EI baths. To achieve this target, attempts have been made in this study to make use of mixed metal oxide (Ru–Ir–Ti-oxide)-coated titanium electrodes. The weight losses of these electrodes during repeated electrolysis, as well as the electrochemical characteristics, have been monitored. In order to prove the efficacy of these inert anodes in industrial production plants, a nickel/cadmium cell was developed using positive electrodes that were developed using the present inert anodes. The cell was formed and cycled 25 times. The resulting data were compared with the performances of a cell with positive electrodes that were prepared using Pt exmet anodes. The results indicate that the performance and stability of the (Ru–Ir–Ti-oxide)-coated

titanium electrodes are similar to those of platinum electrodes.

It is noteworthy that similar (Ru–Ti-oxide)-coated titanium electrodes have been used successfully in chlor-alkali plants for Cl₂ evolution [4,5], in water electrolysis plants, and for CO₂ reduction [6].

2. Experimental

(Ru–Ir–Ti-oxide)-coated titanium exmet electrodes were used in this work. The electrode features were: 12 diamond-shaped openings per inch; true active area: 2.5 cm² per square inch; 7 μm oxide coating thickness: 7 μm; sheet thickness: 1 mm. The titanium sheet was manufactured by the Central Electrochemical Research Institute, Karaikudi. Electrochemical impregnation of nickel plaques was carried out by following the Kandler's method [2] in a 3.2 M Ni(NO₃)₂ solution (pH:2–3.5, specific gravity:1.44) at 80 °C for 1 h. After the EI, the nickel plaques were subjected to a conversion process in 20% KOH solution at 80 °C for 1 h under anodic conditions. After the conversion, the nickel electrodes were washed several times with de-mineralized water until the pH reached about 7. The oxide-coated titanium electrodes and nickel plaques were dried at 100 and 70 °C, respectively.

Electrochemical impregnation was carried out on conventional, sintered-type nickel plaques as well as on fibre-struc-

ture nickel plaques. The main feature of the fibre nickel plaques is a dense network of nickel filaments that is coated with a slurry of nickel and NiO powders. The plaques offer a porosity of up to 90% void volume. These features improve the volume of the deposited active material so that the diffusion of nickel ions into the electrode body is better during the EI.

The variation of the cell voltage with time was monitored during the EI process. Weight losses of the anodes and weight gain of the nickel electrodes were also monitored to estimate the performances of the counter electrodes. For the purposes of comparison, a platinum–titanium counter electrode and a platinum counter electrode were also investigated.

Two series of flooded type 2.85 Ah nickel/cadmium cells were constructed with three positive and four negative plates. One of the cells used positive electrodes with active material that was impregnated from EI baths that contained mixed-oxide-coated titanium counter electrodes. The other cell employed positive electrodes developed from EI baths that contained platinum exmet anodes. Each of the positive electrodes had an active material loading of 1.08 g Ni(OH)₂ · xH₂O per cm³. The negative electrodes for both types of cells were prepared by pasting CdO-active material over fibre-nickel substrates. All nickel electrodes were bagged with a layer of woven nylon separator material. All cadmium electrodes were bagged with Pellon FS2115 non-woven nylon wick material. Each cell was assembled by wrapping the bagged positive and negative electrodes with a Celgard 3400 microporous polypropylene film in a zig-zag fashion and then inserting into a nylon cell container under some pressure. A 35% KOH + 1% LiOH solution was used as the electrolyte; the electrolyte level was about 1 cm above the top edge of the electrodes.

3. Results and discussion

The EI process was performed several times on the fibre as well as on the sintered nickel plaques. The weight loss of the anodes during all processes was found to be of the order of 10⁻⁸ g cm⁻² s⁻¹. These low values of dissolution rates are encouraging, and the dissolution rates for the platinum–titanium and platinum electrodes that are currently employed in the industrial plants are also in the same range.

The weight gain achieved on the fibre-nickel and sintered-nickel plaques as a result of every EI process was found around 10⁻⁵ and 10⁻⁶ g cm⁻² s⁻¹, respectively. This deposition rate is extremely good in the sense that the targeted amounts of active materials can be deposited in the nickel plaques within a few applications of the given EI process. Details of true active area of the cathodes and other relevant data of the EI process on fibre-nickel electrodes are presented in Table 1.

The voltage of the cells during 1 h of the EI normally lies in the 2.5–4.7 V range. The cell voltage generally increases slightly during the impregnation of fibre-nickel plaques, see

Table 1
Data for electrochemical impregnation of fibre-nickel electrodes

EI process no.	Anode exposed area, true (cm ²)	Weight loss of anode (g cm ⁻² s ⁻¹)	Current rate (mA cm ⁻²)		Cathode area, geometric (cm ²)	Weight gain of cathode after conversion (g/%weight gain)	Weight gain of cathode (g cm ⁻² s ⁻¹)	Open-circuit voltage (V)	Voltage, <i>E</i> (0.5 min electrolysis)	Change in <i>E</i> in 60 min
			Anode	Cathode						
1	57.81	5.286 × 10 ⁻⁸	157.00	178.7	50.92	3.4955/23.0	1.888 × 10 ⁻⁵	0.70	3.41	increases to 3.85
4	49.03	2.833 × 10 ⁻⁸	182.25	178.0	50.16	4.0342/25.8	2.083 × 10 ⁻⁵	0.69	3.15	increases to 3.69
8	57.92	1.631 × 10 ⁻⁸	151.85	177.5	49.58	3.5341/22.5	1.977 × 10 ⁻⁵	0.88	3.25	increases to 4.68
11	51.54	5.012 × 10 ⁻⁸	168.80	178.1	48.84	3.3739/23.2	1.916 × 10 ⁻⁵	0.80	3.35	increases to 4.56

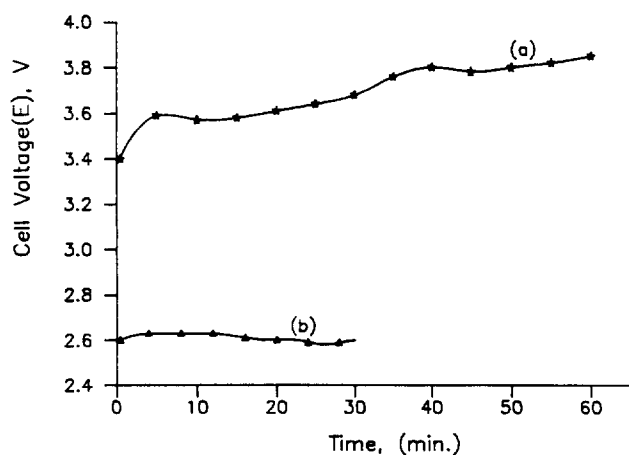
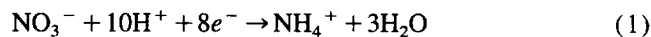


Fig. 1. Variation of cell voltage during electrochemical impregnation of: (a) typical fibre-nickel plaque; (b) typical sintered-nickel plaque. Counter electrode: (Ru–Ir–Ti-mixed metal oxide)-coated titanium exmet.

Table 1 and Fig. 1, curve (a). By contrast, the cell voltage does not change during the impregnation of sintered-nickel plaques, see Fig. 1, curve (b).

When the nickel plaques are dipped in the $\text{Ni}(\text{NO}_3)_2$ solution, the pores are filled with Ni^{2+} and NO_3^- ions. As the current is passed across the cell, the nitrate ions are reduced to NH_4^+ ions [2]



Note that H^+ ions are consumed when reaction (1) takes place. This consumption of H^+ ions is decisive for the impregnation of the porous nickel plaques with $\text{Ni}(\text{OH})_2 \cdot x\text{H}_2\text{O}$. The discharge of the H^+ ions results in a decreased concentration of H^+ ions at the zone of diffusion of the cathode. The pH value of the total electrolyte is kept to a constant value. The longer is the diffusion distance of the H^+ ions, the greater is the decrease in concentration at/within the cathode. As the electrolyte also contains nickel ions (which do not take part in the electrochemical reaction), $\text{Ni}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ precipitates within the electrode after having reached the precipitation pH value. The precipitation starts at the pore areas that are furthest from the surface. The pores will be filled slowly, starting from within. The hydroxides precipitated are, therefore, very finely distributed and suitable for the battery reaction. The complete filling of the pores, i.e., the end of the impregnation process, is recognized by a weak green colouring of the surface and by a rise in resistance of the cathodes.

In the case of fibre-nickel electrodes, when $\text{Ni}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ deposition takes place in the voids where the conductive nickel powder slurry coating is not provided, conductivity decreases and hence the cell voltage increases during the EI, as shown in Fig. 1. A higher 0.5-min electrolysis potential E (about 3.4 V) is observed in case of fibre-nickel plaques. This could arise from the presence of some NiO aggregates inside the pores of the plaques. The NiO may have occluded during the slurry coating.

During the EI, oxygen is evolved at the anode as a result of water oxidation. RuO_2 , by virtue of its ability to form the equilibrium



can promote the oxygen evolution reaction (OER) [7] with minimal loss of electrical energy (overcharge). The holes that are stabilized at the O^- species catalyse the OER efficiently [8]. A solid solution of RuO_2 with TiO_2 and/or IrO_2 would increase the strength of Ru–O bonds because both Ir^{4+} and Ti^{4+} ions enhance the covalent strength [9]. It is this fundamental engineering property that brings the extraordinary external mechanical strength for this triple oxide coating on titanium exmet or sheet.

During the conversion process, the nickel plaques are kept under anodic condition in KOH solution. This would enable: (i) $\text{Ni}(\text{NO}_3)_2$, if adsorbed, to become oxidized to $\text{Ni}(\text{OH})_2 \cdot x\text{H}_2\text{O}$; the NO_3^- ions, thus liberated, would diffuse into KOH solution; (ii) any unleached NH_4^+ ions remaining inside the pores to be leached away in alkali; (iii) $\text{Ni}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ to be converted into the battery-active form.

In order to determine whether the nickel mat electrodes impregnated with the active material $\text{Ni}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ from an EI bath consisting of (mixed-metal-oxide)-coated titanium anodes give a similar performance to that of nickel electrodes developed using platinum anodes, nickel/cadmium cells of capacity 2.85 Ah were constructed with these positive electrodes. The cells were initially subjected to four formation cycles wherein the cells were charged and discharged at the $C/20$ rate initially, and then progressively the rate was increased (up to $C/5$). The cells were then subjected to regular cycling, performed at a $C/5$ charge rate and $C/2$ discharge rate. All charging was carried out by a constant-current method until the correct number of Ah were passed (nearly 40% overcharging was used).

The voltage versus time curves for the 25th cycle of both cells are given in Fig. 2. The charge/discharge characteristics

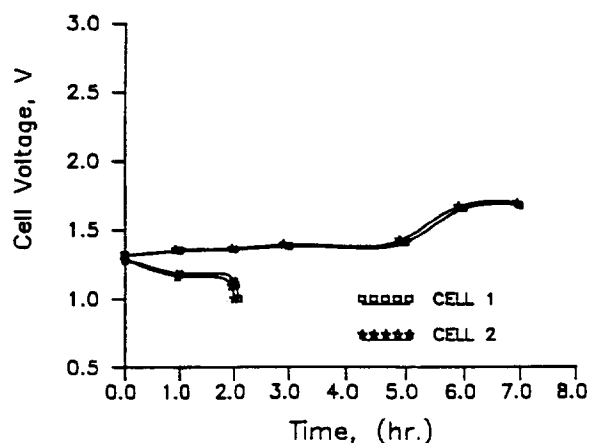


Fig. 2. Charge/discharge curves (25th cycle) of nickel/cadmium cells. Cell 1: positive electrodes developed by employing (Ru–Ir–Ti-mixed metal oxide)-coated titanium exmet anodes in the electrochemical impregnation bath. Cell 2: positive electrodes developed by employing platinum exmet anodes in the electrochemical impregnation bath.

of both cells are virtually identical. This suggests that the performances of the positive electrodes prepared from an electrochemical impregnation bath containing (mixed-metal-oxide)-coated titanium anodes are as good as those of the positive electrodes developed with platinum exmet anodes.

4. Conclusions

(Ruthenium–iridium–titanium oxide)-coated titanium exmet electrodes have been tested as inert anodes in electrochemical impregnation baths that use 3.2 M $\text{Ni}(\text{NO}_3)_2$ solution. Weight losses on these anodes are in the order of 10^{-8} $\text{g cm}^{-2} \text{s}^{-1}$. The cell voltage during the EI process is between 2.5 and 4.7 V, and the electrical energy losses are minimal. The performance of nickel positive electrodes prepared from EI baths with (Ru–Ir–Ti oxide)-coated titanium exmet electrodes exhibit a performance similar to that of positive electrodes prepared with platinum exmet electrodes. Also, the mixed-metal-oxide titanium electrodes do not disintegrate after several EI processes are conducted. All these results suggest that (Ru–Ir–Ti mixed-metal-oxide)-coated titanium electrodes can be deployed as the counter electrodes in the EI baths of nickel/cadmium industrial plants.

Finally, the oxide-coated titanium electrodes are also better electrodes in terms of cost. They are just one-tenth the cost of the platinum electrodes.

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