THE INTERNAL RESISTANCE OF PLASTIC BONDED (PRESSED TYPE) HIGH RATE Ni ELECTRODES*

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Summary

Internal resistance is one of the most important characteristics of Ni–Cd cells. It has a great effect on the discharge voltage, capacity, and high rate behaviour. In this paper we report the results of an investigation in connection with the internal resistance of the plastic bonded Ni electrode and its variation as a function of pressure and high rate cycling.

Introduction

The high rate behaviour of Ni–Cd cells is largely influenced by the internal resistance of the Ni electrode. The main reason for this is to be found in the semiconducting properties of the nickel oxides, especially the Ni(II) oxide. Therefore it is very important to know exactly the resistance of both the active material and the plastic bonded electrode constructed from it, in which the semiconducting oxides are intimately mixed with an insulating plastic material [1, 2]. Several papers have already dealt with the internal resistance measurement of Ni–Cd cells and its variation during use [3 - 6, 8].

Our present work deals with an investigation of plastic bonded electrodes developed in our laboratory, and measurement of the variation of the impedance of the electrode as a function of load, pressure, and high rate cycling.

Effect of pressure on the internal resistance of Ni electrode

Our investigations were fundamentally directed to the determination of the resistance of a PTFE–Ni–carbon mixture as an electrode material. Its approximate composition was: 15% carbon black, 15% graphite, 10% PTFE and 60% $Ni(OH)_2$. The electrodes were produced by pressing the mixture at

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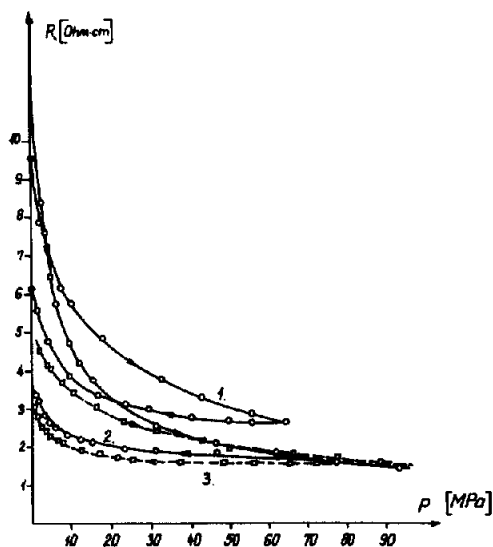Fig. 1. Variation of internal resistance with pressure.

120 MPa/cm^2 into a former to produce a 105 × 42 × 2.5 mm plate. A Ni screen (60 μm wire, 100 μm hole) was pressed on both sides of the electrode as a current collector.

The conductivity was determined by d.c. measurements using an LDA type ammeter and a digital multimeter with an input resistance of 10^8 Ω. Measurement error was ± 5%.

Variable pressures were applied to the surface of the dried electrode and the resistivity was determined before, curve 1, and after 3 charge–discharge cycles, curve 2, Fig. 1.

The Figure shows that during forming, the internal resistance decreases slightly at first and then remains constant. The resistance as a function of pressure decreases up to 60 MPa, but above this pressure it hardly changes.

The reproducible hysteresis between the resistivity on charge and discharge is paralleled by a change of about 25% in sample thickness. This can be explained on the basis of the particle model reported by us in a previous paper [7]. According to this model the conductivity occurs between the individual particles (carbon black, graphite, and active material) of the electrode bonded by the plastic material.

Thus useful information is obtained concerning the relation between the discharge load and the structure of the electrode during its service life.

Investigations of electrode impedance

A number of procedures are available for separating the ohmic and non-ohmic parts of the impedance. That of the Ni electrode can be obtained by
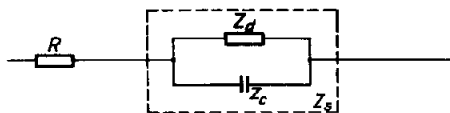
Fig. 2. Circuit replacing electrode processes in Kordesch—Marko measurement method.

the approximate equivalent circuit (Fig. 2) where R represents the ohmic portion, Z_c the double layer capacity (relating to the charge transfer potential), Z_d the diffusion related impedance, and Z_s the sum of the non-ohmic parts relating to the kinetic inhibition of the electrode reaction processes.

According to the Kordesch—Marko method [8], on interrupting the discharge current a sudden potential drop appears in the ohmic portion of the impedance, which is followed by a slower potential variation characteristic of the non-ohmic impedance; in this way the two parts can be separated.

The samples used for these measurements had the same composition and size as those previously employed.

Two nickel and three cadmium electrodes were connected in a cell the nominal capacity of which was 3.9 A h. The electrolyte was 1.2 s.g. aqueous KOH containing 15 g/l of LiOH.

Characteristic potential—time traces are given in Fig. 3. Such traces were taken and evaluated after different periods of high rate cycling, the conditions of which were:

Charging with $I = 0.7 \, C_5$ (2.8 A) for 3 h 50 min;
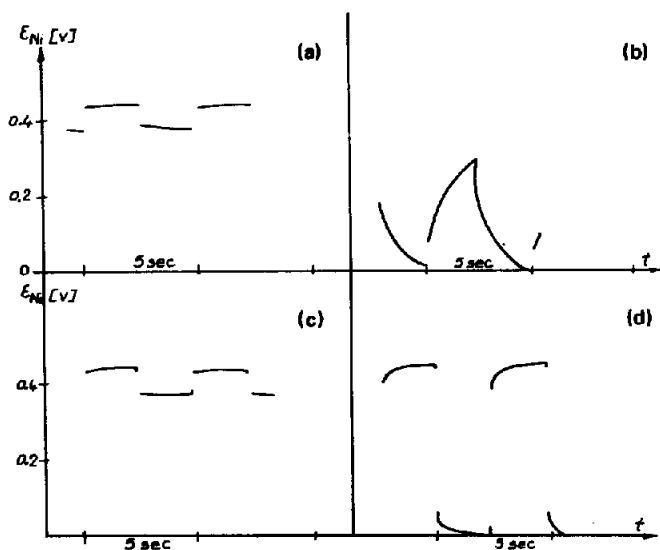discharging with $I = 3 \, C_5$ (12 A) for 10 min.

Fig. 3. Potential variation arising on discharge current interruption as a function of time.
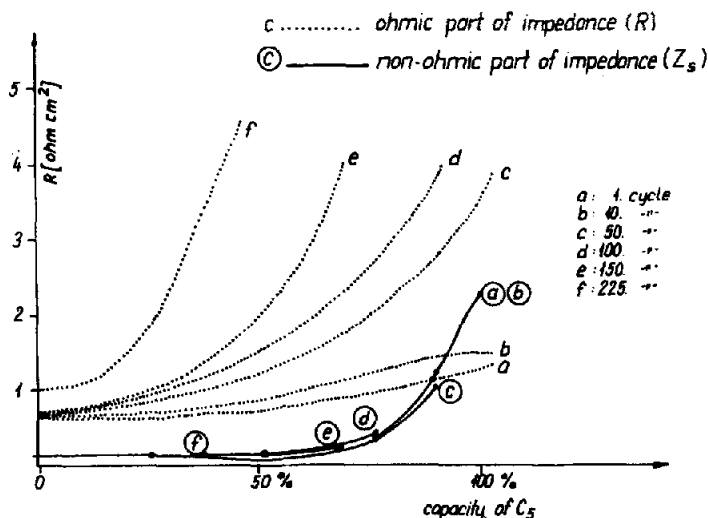
Fig. 4. Change of ohmic and non-ohmic parts of the impedance of the Ni electrodes.

The measurements were made with a discharge current of $I = 3\ C_5$ (12 A) to zero potential of the Ni electrode against an Hg/HgO 6N KOH reference electrode, frequency of interruption: 2×10^{-1} Hz. The variation in potential was recorded on a Bryans X–Y–t recorder. The results are shown in Fig. 4.

It can be seen from this Figure that during cycling the ohmic part of the impedance increases while the non-ohmic portion is practically unchanged. The result, that the non-ohmic part — characteristic of charge transfer and diffusion — does not change, means therefore that the transport of material in the electrolyte and the structure remain unchanged during the life test.

This fact is confirmed by porosity measurements and other experiments given in another publication [8].

The high rate cycle life obtained (150 - 250 cycles) is similar to that of good quality pocket type electrodes and proves the utility of the plastic bonded electrodes.

Conclusion

The measurements have proved that the internal resistance of plastic bonded electrodes depends to a great extent on the external pressure, and the changes in it can be described by a hysteresis curve.

The deterioration of the electrodes examined during a high rate cycle life test is a consequence of the increase in the ohmic part of the impedance, while the non-ohmic part, concerned with diffusion and the kinetics of charge transport, is practically unchanged.

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