

PLASTIC BONDED ELECTRODES FOR NICKEL-CADMIUM ACCUMULATORS.

III. INFLUENCE OF ACTIVE LAYER COMPOSITION ON GALVANOSTATIC AND POTENTIOSTATIC DISCHARGE CURVES

B. KLÁPŠTĚ, J. MRHA, K. MICKA, J. JINDRA and V. MAREČEK

J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 102 00 Prague 10 (Czechoslovakia)

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Summary

Studies on the addition of a conducting component (carbon black, graphite, carbonyl nickel) and poly(tetrafluoroethylene) as binder to the active material used in pocket-type nickel oxide electrodes have shown that the second discharge step, which is observed in the discharge curve of a pressed nickel oxide electrode in the potential range from -100 to -600 mV (Hg/HgO), can be markedly influenced or fully suppressed as in the case of a sintered nickel oxide electrode. The existence of this discharge step is attributed to differences in the ohmic contacts of the electroactive particles in the pressed electrode.

Introduction

The complicated electrochemical mechanism of the nickel oxide electrode in alkaline accumulators is manifested also by the form of the polarization ($E-t$) curves characterizing the charging and discharging process. Their position with respect to each other corresponds to a typical hysteresis curve [1] and the potential difference between the anodic and cathodic step depends on the type of nickel oxide electrode as well as on the thickness of the active layer [2, 3].

That different experimental techniques of different authors often led to different results suggests that the method of preparation and testing of the nickel oxide electrode influences its electrode mechanism. This influence is shown by the formation of various steps in the cathodic $E-t$ curve in addition to the main step, which is made use of in alkaline batteries and is located in the potential range $0.25 - 0.35$ V vs. the Hg/HgO electrode in the same electrolyte. The other step described in the literature [4 - 14] is at -100 to -600 mV according to the type of electrode and current load.

The reasons for the existence of the more negative step in the discharge curve have not been adequately explained and, in respect of the complexity of the nickel oxide electrode, it is questionable whether adequate explanation can be offered at all. According to certain authors [4, 8 - 10], the second discharge step is attributed to the reduction of dissolved or trapped molecular oxygen, especially in the presence of graphite; according to others [5, 7, 11, 13, 14] it is attributed to the reduction of lower nickel oxides, or to the reduction of oxygen to peroxide which participates in the reduction of nickel oxide [12].

The research work on the mechanism of the nickel oxide electrode has been carried out on commercial electrodes and on films of variable thickness prepared by electrochemical or chemical deposition on a conducting substrate. Only commercial sintered electrodes did not give a second discharge step, whereas pocket-type electrodes and deposited oxide films did so, although to a different extent. These facts suggest that the second discharge step depends largely on ohmic conditions in the electrode [15, 16]. The present work presents evidence to verify this supposition.

Experimental

Test electrodes were prepared by pressing the electrode mix at 60 MPa into the form of a circular tablet which was then wrapped in a fine nickel gauze (0.05 mm dia. wire, 0.08 mm mesh, 0.285 kg/m² square mass) and pressed again at 100 MPa. Its diameter was 10 mm.

The main component of the electrode mix was the commercial powdered active mass KBL [15, 16] containing 43 - 47% nickel as hydroxide and 16 - 19% graphite, VA. This active mass is manufactured in Czechoslovakia for pocket-type electrodes by Lachema, Bohumín. Our electrodes contained 0.3 g of this material, corresponding to a theoretical capacity (for a one-electron reaction step) $C_t = 64$ mA h at a determined nickel content of 47%.

Other components were acetylene black P-1042 (VEB Stickstoffwerke, Piesteritz, GDR), or Teflonised carbon black, prepared by depositing PTFE from aqueous suspension (PTFE dispersion GP-1 or GP-2, ICI, England), on the P-1042 carbon black; the product contained 35 - 75% PTFE (denoted as S-35 to S-75), additional graphite VA (Rudné doly, Týr n. Vltavou), which, according to sedimentation analysis contained particles in the range 10 - 200 μ m without a marked maximum (the remainder on a 0.16 mm mesh was at least 45%), and Type 255 carbonyl nickel powder (INCO, England), as used in the preparation of sintered nickel electrodes. The conductive components were added either alone or mixed with powdered PTFE (Fluon CD-1, ICI, England) in similar proportions to the case of carbon black, *i.e.*, 35 - 75% PTFE.

Comparative measurements were carried out with a commercial sintered nickel oxide electrode whose theoretical capacity was similar to that of the pressed electrodes.

The counter electrode was a nickel sheet, which ensured an equal current load on both sides of the test electrode. The reference electrode, to which all potentials are referred, was Hg/HgO in a solution of potassium hydroxide (density 1.2 g/cm^3) which was used in all electrochemical measurements.

The test electrode was first charged (20 h at 6 mA) and then the discharge $E-t$ curve was recorded up to the potential of hydrogen evolution (about -1.1 V). Usually, after 3 - 5 cycles, the discharge characteristic was satisfactorily reproducible from cycle to cycle.

Some measurements were made in the potentiostatic regime with the use of a PS-20 type potentiostat combined with a PV-1 controller (Forschungsinstitut Meinsberg, GDR). The potential sweep rate was 6.67 mV/s , the potential pulse was of a triangular form and only the cathodic part of the curve was recorded.

The potential sweep rate in cyclic voltammetry was 50 mV/s in both directions with 20 s delays at both potential limits, namely -500 and $+575 \text{ mV}$.

Results and discussion

The discharge characteristics of electrodes containing the pure KBL active mass without, or with, addition of a conductive component, are shown in Fig. 1 with carbon black, in Fig. 2 with graphite, and in Fig. 3 with carbonyl nickel. A comparison of these three conductive components at equal content in the mix (91.4% KBL, 8.6% conductive component) is shown in Fig. 4. It is seen that the addition of a conductive component always causes an increase in the electrode capacity measured up to the potential of hydrogen evolution, namely, from 77% C_t for pure KBL to 87 - 93% C_t for the G_2 carbon black mix. When the discharge characteristics were measured at the lower load of 8 mA, the corresponding capacities were 84, 89, 95, and 99% C_t for the mixtures A, G_1 , G_2 , and G_3 , respectively. The fraction of the capacity corresponding to the second discharge step increases in the same order.

The shape and position of the discharge curve are also influenced. The first discharge step (up to the potential of 0 to -0.2 V) becomes more horizontal after the addition of the conductive component, *i.e.*, more akin to that of the sintered nickel oxide electrode (Figs. 1 - 3). This is apparently due to an improvement in the conductivity of the active mass, *i.e.*, smaller ohmic losses (iR).

The influence of the conductive component on the second discharge step is still more marked: it is shifted to more positive potentials (from -0.5 V for KBL to -0.3 to -0.15 V for the mixtures), again as a result of smaller ohmic potential losses.

We can distinguish two types of conductive component: carbon black as a typically voluminous one (bulk density 0.04 g/cm^3) and graphite or

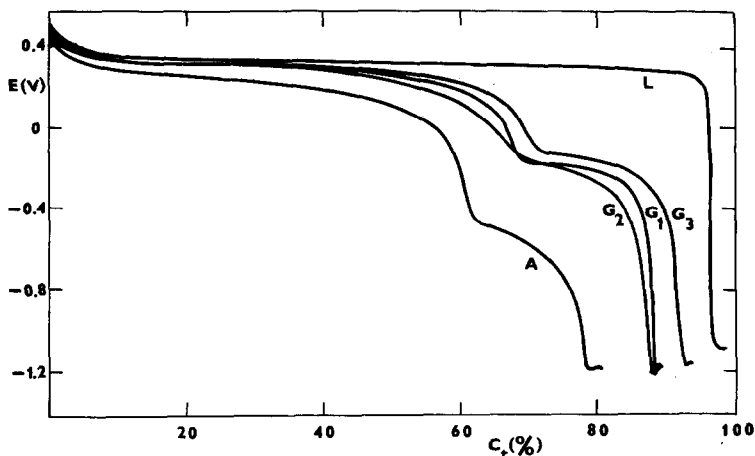


Fig. 1. Galvanostatic discharge curves for pressed electrodes of 10 mm diameter at a discharge current of 50 mA at different ratios of KBL/acetylene black = P: A, KBL; G_1 , P = 26.1; G_2 , P = 10.6; G_3 , P = 4.6; L, sintered electrode.

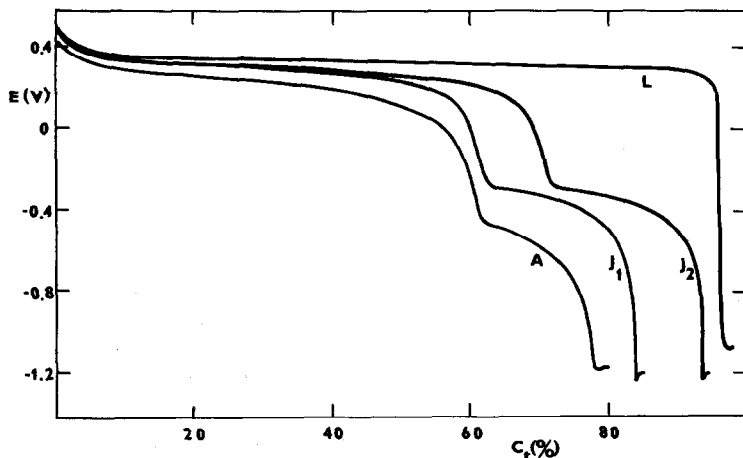


Fig. 2. As Fig. 1, but at different ratios of KBL/graphite VA = P: A, KBL; J_1 , P = 10.6; J_2 , P = 4.6; L, sintered electrode.

carbonyl nickel as typically compact materials (bulk densities 0.54 and 0.77 g/cm³). The black forms, as a result of its large volume and small particles, a perfect space lattice which provides transport of electrons to all oxide particles. This results in a shift of the second discharge step to more positive potentials, and in a more smooth transition from the first to the second step than with pure KBL or with graphite or carbonyl nickel (Fig. 4). Because of the high dispersion of the black, the effect of a change in content is not so marked as with graphite or carbonyl nickel (compare Fig. 1 with Figs. 2 and 3).

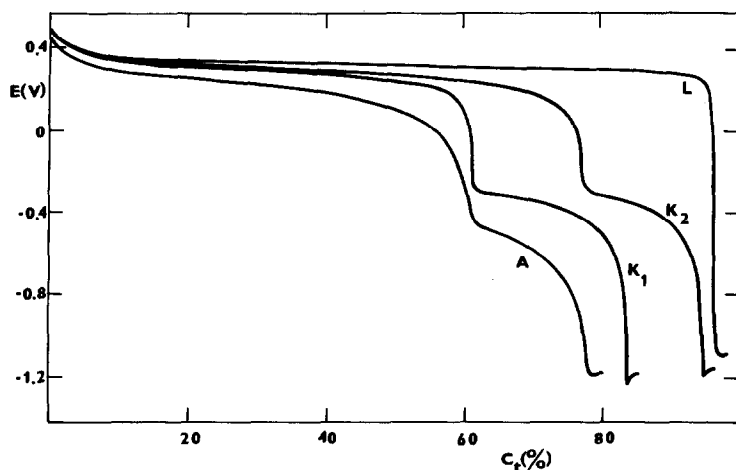


Fig. 3. As Fig. 1, but at different ratios of KBL/carbonyl nickel INCO 255 = P: A, KBL; K_1 , P = 10.6; K_2 , P = 4.6; L, sintered electrode.

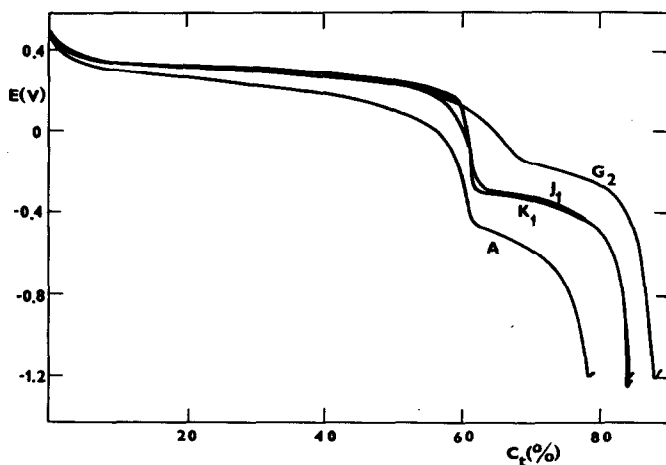


Fig. 4. As Fig. 1, but at constant ratio of KBL/conductive component = 10.6: A, KBL; G_2 , carbon black; J_1 , graphite VA; K_1 , carbonyl nickel INCO 255.

The influence of the addition of PTFE (the ratio of KBL to PTFE was in all cases 8:1) is seen from Figs. 5 - 8. The electrical conductivity of the KBL-carbon black-PTFE mix (Fig. 5) is obviously worse (especially for mix B_1 or B_4) than for the KBL-carbon black mix (Fig. 1), since the first discharge step has a falling tendency and the electrode capacity is lowered from 87 to 93% C_t (Fig. 1) to 84% C_t (Fig. 5). For this reason the second discharge step is less-well defined. Decreasing the content of KBL in favour of carbon black in the presence of PTFE (mix B_5) causes a marked shift of the discharge curve to more negative potentials and a lowering of the elec-

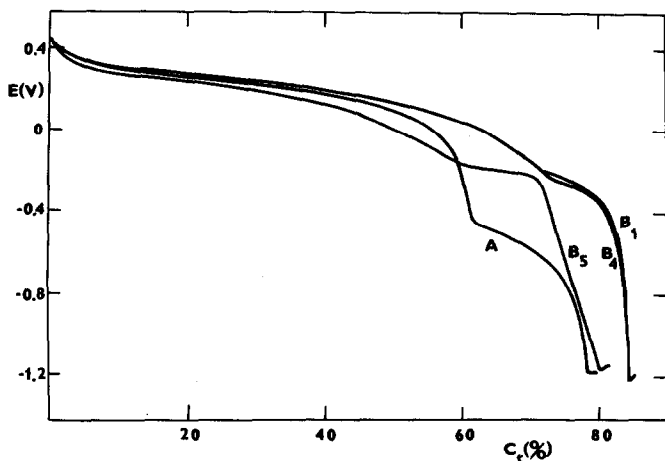


Fig. 5. As Fig. 1, but with different contents of PTFE in the PTFE-acetylene black mixture: A, KBL; B₁, 75% PTFE; B₄, 55% PTFE; B₅, 35% PTFE (cf. Table 1).

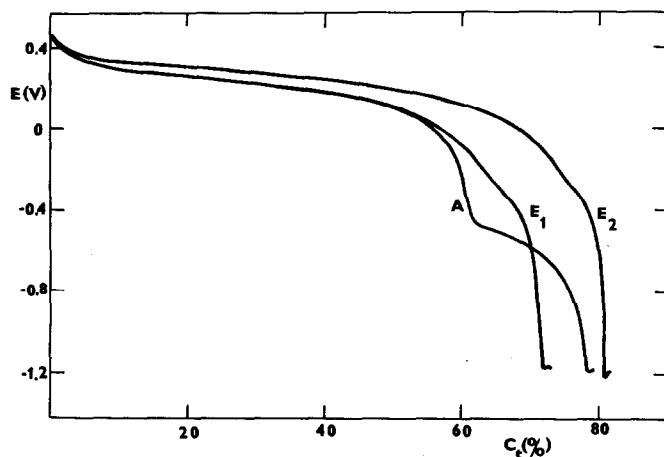


Fig. 6. As Fig. 1, but with different contents of PTFE in the PTFE-graphite VA mixture: A, KBL; E₁, 55% PTFE; E₂, 35% PTFE (cf. Table 1).

trode capacity to a value corresponding to pure KBL. The increased content of Teflonised acetylene black apparently causes an increase in the volume fraction of hydrophobic pores at the expense of the hydrophilic ones, whereby the transport of ions in the pores is hindered and some electroactive particles are excluded from the electrode reaction.

The discharge characteristics of electrodes containing KBL, graphite and PTFE, or KBL, carbonyl nickel and PTFE are mutually similar (Figs. 6 and 7), as was also the case for analogous mixtures without PTFE (Figs. 2 and 3). By contrast with acetylene black (Fig. 5), increasing the content of these conductive components favourably influences the discharge capacity

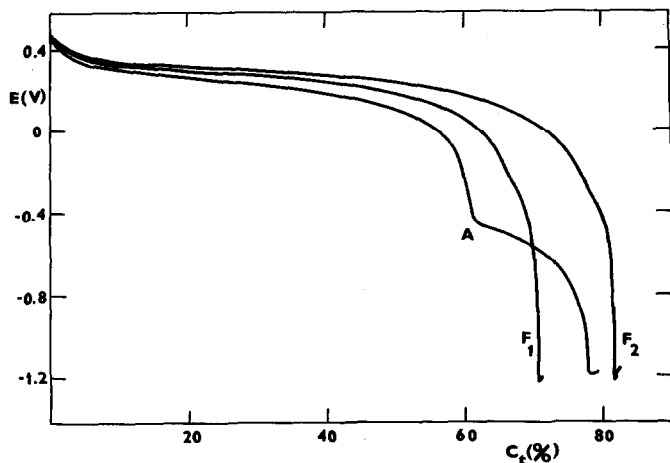


Fig. 7. As Fig. 1, but with different contents of PTFE in the PTFE-carbonyl nickel INCO 255 mixture: A, KBL; F_1 , 55% PTFE; F_2 , 35% PTFE (*cf.* Table 1).

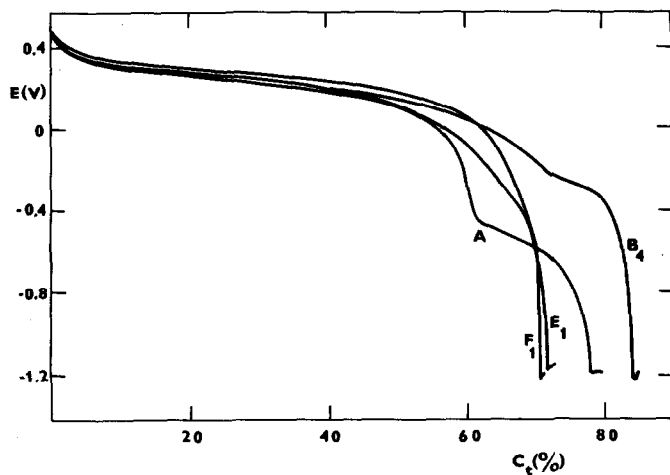


Fig. 8. As Fig. 1, but at constant content of PTFE in the PTFE-conductive component mixture equal to 55%: A, KBL; B_4 , acetylene black; E_1 , graphite; F_1 , carbonyl nickel INCO 255 (*cf.* Table 1).

(Figs. 6 and 7); their lower dispersion obviously does not allow the formation of such a perfect space lattice as with the acetylene black. It is seen from these figures that in the presence of PTFE and graphite or carbonyl nickel the second discharge step is almost fully eliminated, and the capacity corresponding to pure KBL could be attained only with an increased content of the conducting component (mix E_2 or F_2). The influence of the conducting component in the mixture with KBL and PTFE at a constant composition is best illustrated by Fig. 8 showing various modifications of the second discharge step.

TABLE 1

Composition of electrode mixtures

The contents of active mass KBL, conductive component, and PTFE in mass percent, are denoted as p_1 , p_2 and p_3 , respectively; $p_4 = 100p_3/(p_2 + p_3)$.

Mix	KBL p_1	Type of conductive component	PTFE			p_1/p_2
			p_2	p_3	p_4	
A	100	—	—	—	—	—
B ₁	86.5	ac. black	3.4	10.1	75	26.1
B ₄	82.5	ac. black	7.9	9.6	55	10.6
B ₅	75.0	ac. black	16.2	8.8	35	4.6
E ₁	82.5	graph. VA	7.9	9.6	55	10.6
E ₂	75.0	graph. VA	16.2	8.8	35	4.6
F ₁	82.5	INCO 255	7.9	9.6	55	10.6
F ₂	75.0	INCO 255	16.2	8.8	35	4.6
G ₁	96.3	ac. black	3.7	—	—	26.1
G ₂	91.4	ac. black	8.6	—	—	10.6
G ₃	82.2	ac. black	17.8	—	—	4.6
J ₁	91.4	graph. VA	8.6	—	—	10.6
J ₂	82.2	graph. VA	17.8	—	—	4.6
K ₁	91.4	INCO 255	8.6	—	—	10.6
K ₂	82.2	INCO 255	17.8	—	—	4.6
L		sintered Ni electrode	—	—	—	—

The polarization resistance, R_p , of the pressed electrode is much higher in the second discharge step than in the first one. For electrodes containing 82.5% KBL, 9.6% graphite (particles in the range 3 - 6 μm), and 7.8% PTFE we measured, in the current density range 6.4 - 25.5 mA/cm^2 , the potential shift of the $E-t$ discharge curves and calculated $R_p = 3.6 \Omega \text{ cm}^2$ for the first and 7.2 $\Omega \text{ cm}^2$ for the second discharge step.

The existence of the second discharge step cannot be attributed, as some authors suppose [4, 8 - 10], to the reduction of oxygen trapped or adsorbed in the pores, since the charge passed in this step is too large.

The nickel oxide electrode is formed by a space lattice of electroactive particles; different modes of preparation of such electrodes lead to different degrees of connection of these particles both with one another and with the current collector. In the case of sintered electrodes, the form of the cathodic $E-t$ curve allows us to suppose that all electroactive particles of nickel hydroxide, deposited on the surface of the conducting matrix, have approximately the same quality of contact. This system can be illustrated by a model scheme according to Fig. 9(a). Thus, the electroactive particles are either in direct contact with the current collector or via a particle of carbonyl nickel, which is a perfect conductor. Since both these modes of contact are practically equivalent, there is no difference between them regarding the ohmic potential drop.

In the case of a pocket-type electrode, which contains a mixture of powdered nickel hydroxide and a conductive component (graphite or

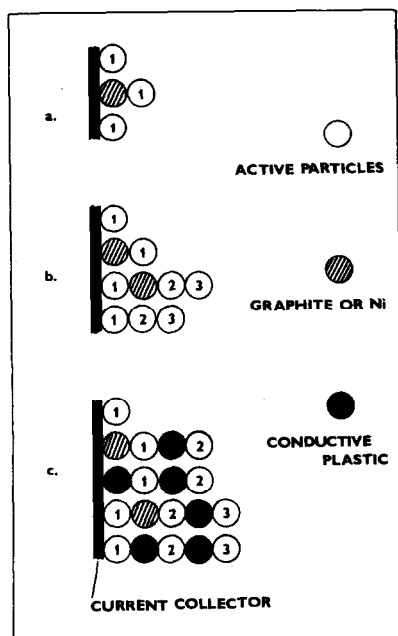


Fig. 9. Schematic illustration of ohmic conditions in active layer of (a) sintered, (b) pocket-type, and (c) plastic bonded electrode.

nickel), all electroactive particles cannot function under equal conditions since there is no continuous, conducting space lattice which would enable equal participation of all electroactive particles. According to their contact with the collector, three groups can be distinguished (Fig. 9(b)). Electroactive particles 1 have, as in a sintered electrode, perfect contact and their $E-t$ curve would show only one step. The functioning of particles 2 is conditioned by the conductivity of particles 1, which form an intermediate step in their contact with the collector. This circumstance has an influence on the electrochemical behaviour of particles 2. Particles 3 have, accordingly, an even less acceptable position, and are the cause of the decreased performance of the electrode with respect to expectation. Their presence may explain why the second discharge step is formed in the $E-t$ curve.

The introduction of the plastic binder, which is made conductive by the addition of either acetylene black, graphite or carbonyl nickel, changes somewhat the structure of the active layer, which can be modelled according to Fig. 9(c). The main difference is that by virtue of the conducting plastic network particles 2 can participate in the electrode process either in the first discharge step ($E-t$ curve with a single potential delay), or partly in the modified second step. A fraction of particles 3 can also, under favourable contact conditions, take part in the electrode process, whereby the utilization of the active mass is improved.

The concept of ohmic control of the participation of nickel hydroxide particles in the electrode reaction was supported by the following experiments, illustrated by Figs. 10 and 11.

In Fig. 10 are shown the potentiostatic curves obtained with a pressed electrode (curve A for pure KBL, B₄ for KBL with acetylene black and PTFE) and a sintered electrode (curve L). It is seen that the addition of the black and PTFE to the active mass causes an increase of the current maxima corresponding to both discharge steps of the nickel oxide electrode. These maxima become not only higher but also closer to each other, hence, the KBL-acetylene black-PTFE mix becomes similar in character to the sintered electrode, which is characterized by a single current maximum.

A model electrode was achieved by connecting, in parallel, two sintered nickel oxide electrodes. The potentiostatic curve obtained shows only one cathodic and one anodic current maximum (Fig. 11, curve 1). However, when this model electrode was modified by adding a series resistance $R = 10 \Omega$ to one of the sintered electrodes, the resulting potentiostatic curve (Fig. 11, curve 2) had two cathodic current maxima, since the polarization of the two electrodes in the system differed by IR . This supports our concept of ohmic control of the electrochemical reaction of pressed nickel oxide electrodes.

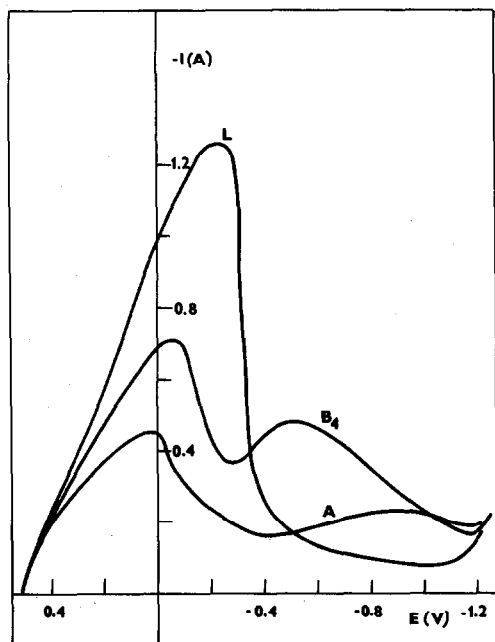


Fig. 10. Potentiostatic $i-E$ curves for pressed electrodes of 10 mm diameter and a sintered electrode at a potential sweep rate of 6.67 mV/s: A, KBL; B₄, KBL with acetylene black and PTFE (Table 1); L, sintered electrode.

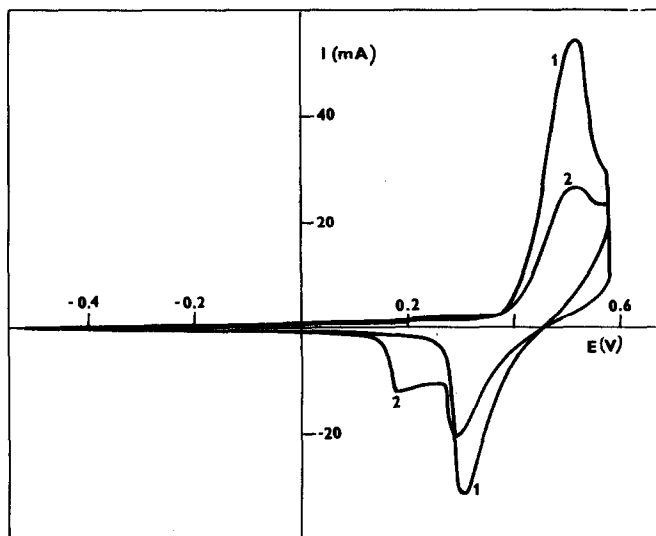


Fig. 11. Potentiostatic i - E curves for a model electrode from two equal sintered Ni electrodes connected in parallel at a potential sweep rate of 50 mV/s: 1, without resistance; 2, a series resistance of 10 Ω was added to one of the electrodes.

Conclusions

Our experiments showed that the parameters of plastic bonded nickel oxide electrodes can be controlled to a large extent by the type and quantity of the conductive component, which influences the degree of participation of electroactive particles in the electrode reaction. PTFE particles function only as binder and improve the rolling properties of the electrode mix [15, 16]. Conditions of ohmic contact among individual particles influence the formation of the second discharge step.

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