Overcharge protection of MnO_2 cathodes

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Abstract

A test cell has been developed to examine some metal oxides for their possible application as active oxygen-evolving materials. The tests were run with doped MnO_2 electrodes in 9 M KOH and applying current densities up to 10 mA/cm^2. The most effective additives were vanadium pentoxide (V_2O_5) (if applied in higher concentrations), nickel cobaltites ($NiO \cdot Co_2O_3$ and $NiO \cdot 2CoO$) and the cobalt-spinel Co_3O_4. These compounds were able to convert electrical charges to oxygen with an efficiency close to 100%. The promoted oxygen evolution prevents the oxidation of the MnO_2 electrode to soluble manganates subsequently disproportionating to Mn(IV) and Mn(II) causing a loss of active material because the latter will not be re-oxidized to Mn(IV) on charge.

Introduction

The manganese dioxide cathode is one of the most useful electrodes for primary cells as well as for rechargeable systems. Depending on the projected use of the manganese dioxide electrode, electrochemists tried to improve the performance by different means. Not only was the production process studied very carefully for influencing the properties of the product in a positive way, the possibilities of changing the material by subsequent thermal or chemical treatments were also evaluated.

The most important target for the use of 'modified' manganese dioxide in primary cells was to increase the electrode capacity for one single discharge. Rechargeable systems require the stability of the electrode for many discharge and charge reactions without losing more than a negligible fraction of its capacity.

The most common methods for chemical modification of manganese dioxide are: the ion exchange method [1, 2], the co-precipitation method [2, 3], the electrochemical co-deposition [4], the admixture of other oxides with or without a thermal treatment [5–7], and the addition of earth alkali hydroxides [8] before pressing the cathodes.

Other reasons for special treatments of manganese dioxide are the capability to consume evolved hydrogen [9] or the change of overcharge

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reactions. The main goal of the following work was to achieve a transformation of input charge to oxygen with an efficiency close to 100%. Complex oxides containing Co, Zn, Al, Ni, and others were expected to be useful [10–14] as well as synthetic perovskites which were tested for similar operations [15, 16].

The evolution of oxygen seems to be the only way to prevent the formation of manganates(VI, VII) without limiting the voltage of the charger. The manganates influence the cycle life of the cathode because they dispropor-tionate to compounds of Mn(IV) and Mn(II). The latter are not reoxidized in the next charging process and thus are lost for the cell capacity. The oxygen may be recombined with the hydrogen produced at the zinc anode to form water and the only overcharge reactions are the decomposition and re-production of water [17, 18].

Experimental

Preparation and characterization of oxides

The following oxides were taken into account for use as additives to manganese dioxide cathode mixtures:

1. $CoAl_2O_4$ ($= CoO \cdot Al_2O_3$)
2. $ZnCo_2O_4$ ($= ZnO \cdot Co_2O_3$)
3. $NiCo_2O_4$ ($= NiO \cdot Co_2O_3$)
4. V_2O_5
5. NiO
6. Co_3O_4
7. $NiO \cdot 2CoO$

Except the vanadium pentoxide, the nickel(II) oxide, and the cobalt(II, III) oxide which were available in reagent grade purity (MERCK No. 824, 6723, and 2544), the required compounds were prepared either by mixing aqueous solutions containing the nitrates of the oxide forming metals in stoichiometric ratio, evaporizing the water, and heating the residue for at least 3 h at a temperature of 850 °C in the presence of air or by co-precipitation of the hydroxides and subsequent drying and heating of the solid overnight.

The products were tested by X-ray inspection to see how much of the material was present as a mixture of single oxides and how much was converted to a spinel-type compound. As a result of this investigation the spinel-type structure of the compounds nos. 1–3 and 6 was confirmed with the additional remark that compound no. 3 contained a certain amount of free nickel oxide. Consequently, the activities of nickel(II) oxide, the pure cobalt-spinel Co_3O_4, and a nickel(II)–cobalt(II) oxide (no. 7) had to be tested. The X-ray characterization of compound no. 7 is presented in Fig. 1.

Preparation of electrodes

The MnO_2 electrodes were prepared using the following materials:
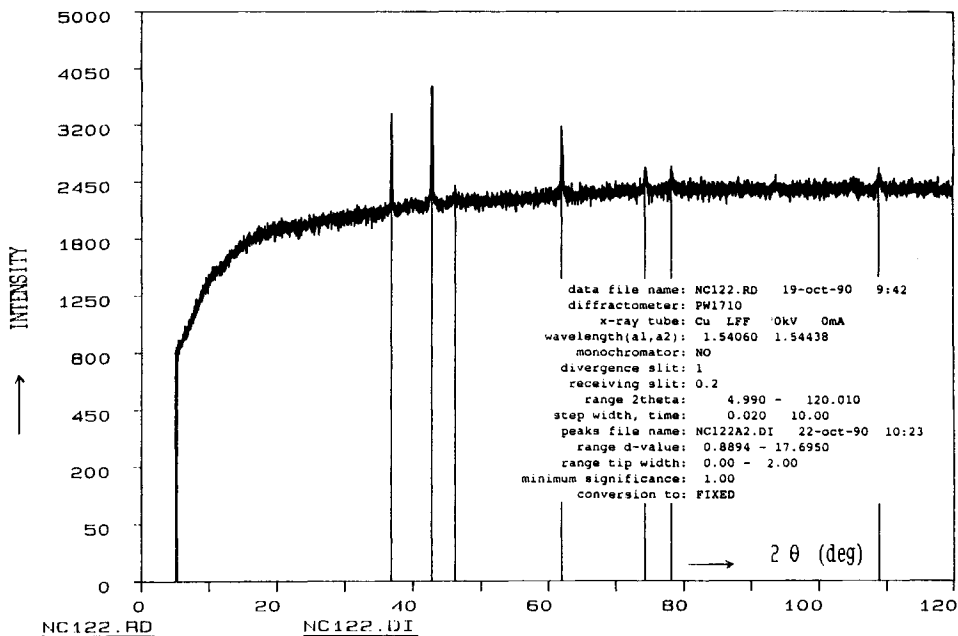(1) electrolytic manganese dioxide (EMD), Mitsui, IBA-sample No. 18

Fig. 1. X-ray diffraction pattern for NiO·2CoO.

(2) graphite powder, Lonza, KS 44, IC-sample No. 1
(3) Hostaflon powder, Hoechst, PTFE 2071.
The basic mixture was 82% EMD, 10% graphite, 8% Hostaflon. After dry mixing these components (+ additives) for 12 h, the powder was immersed in benzine (boiling range 80–110 °C) and homogenized for 3–4 h. Subsequently the excess of benzine was separated by filtration and the solid residue was kneaded until the paste had a suitable consistency for the following rolling process. Rolling started with a sheet of about 4 mm (thickness) and was continued step by step until a final thickness of 0.8–0.9 mm was achieved. In the last step the foil was rolled on a nickel screen used as a current collector. Finally the product was dried at 40 °C for 12 h. Circular electrodes with a diameter of 50.5 mm were cut out (4–5 g of active mass, geometrical area 20 cm^2), contacted with a nickel wire, and used as working electrodes in the test cell.

Conduction of tests
    The overcharge tests were performed using a special cell construction presented in Fig. 2. The cell consisted of two plates made from polymethacrylate ('plexiglas') which were assembled by four screw bolts. Both plates were prepared for the adjustment of a circular electrode and an electrolyte compartment by a milling process. The housing of the working electrode (MnO_2 with additive) and the reference electrode (Zn wire) was fitted with a tube system for gas collection.
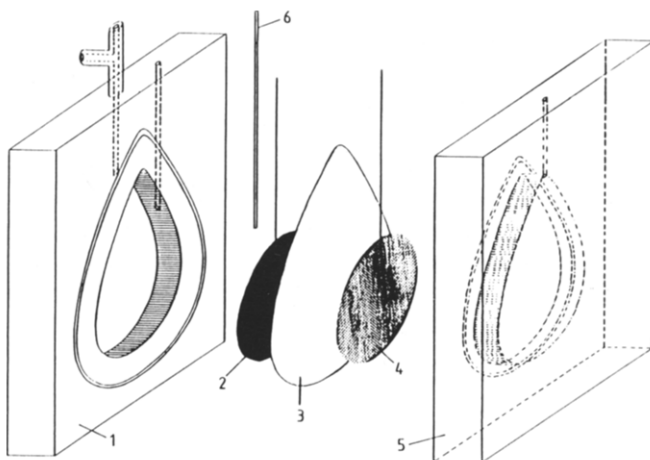
Fig. 2. Test cell for overcharge experiments. 1, 5, Cell block with electrolyte space; 2, working electrode; 3, separator; 4, counter electrode; 6, reference electrode.
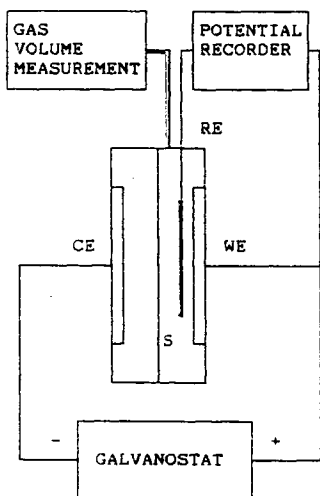

Fig. 3. Test arrangement. WE, working electrode; CE, counter electrode; RE, reference electrode; S, separator.

The cell stack containing an additional separator sheet between the two plates was made gastight by means of two o-rings with a particular geometry. The electrolyte compartment containing the counter electrode (nickel screen) was vented to let the produced hydrogen escape. On the other side the evolved oxygen was collected and its volume was recorded.

After fixing the electrodes and assembling the cell the electrolyte compartments were filled with 9 M KOH, the reference electrode was inserted, and the electrodes were connected with a galvanostat (WE = +, CE = −) and a potential recorder (WE = +, RE = −). The working electrodes were

applied in 90–95% charged condition (as they were produced) and this means that the overcharge reactions started nearly as soon as the cell was powered by the galvanostat. In the ideal case (efficient additive) the oxygen evolution curve followed the pre-calculated track with practically identical slope. Only a small number of tests included a discharge period of the working electrode to detect possible changes in its performance. A manganese dioxide electrode without additive was used as a standard.

In addition to the volumetric measurement of the evolved oxygen, the potential of the working electrode versus a zinc reference electrode was recorded.

The complete test set-up including the electrical circuits as well as the gas collecting device is shown by Fig. 3.

Results and discussion

The first series of experiments was started to establish the properties of an undoped MnO_2 electrode comparing it with electrodes containing 5% of doping oxide. As Fig. 4 shows, the amount of evolved oxygen is significantly different and clearly dependent on the nature of the added oxide. The only exception is found in curve no. 3 (zinc cobaltite, $ZnO \cdot Co_2O_3$) which is close to curve no. 1 (undoped MnO_2) and shows no advantage from this additive.
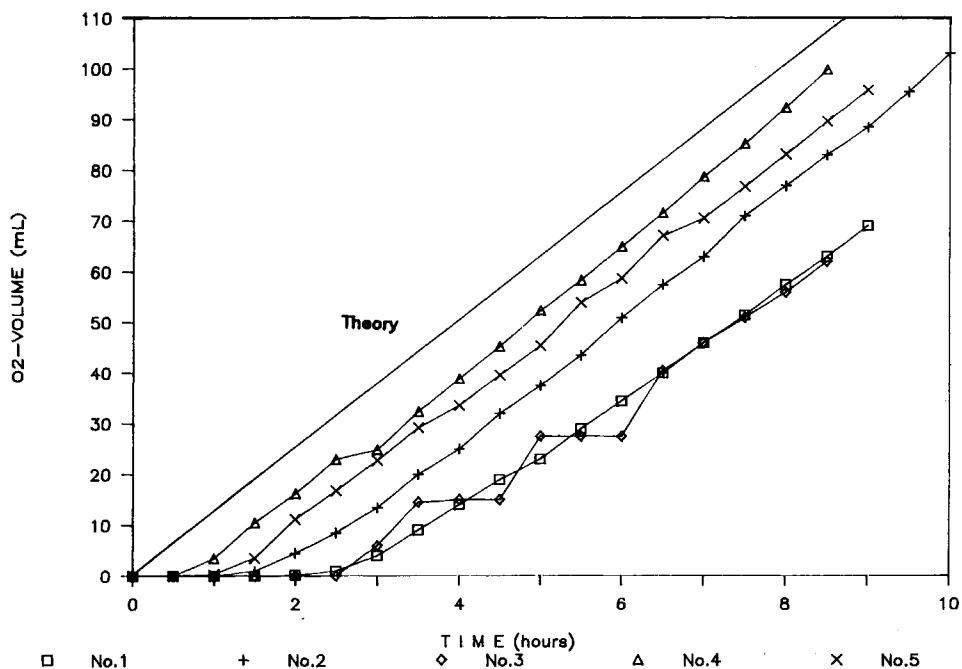

Fig. 4. Oxygen evolution from MnO_2 electrodes. No. 1: pure MnO_2 (=reference), No. 2: 5% $CoO \cdot Al_2O_3$, No. 3: 5% $ZnO \cdot Co_2O_3$, No. 4: 5% V_2O_5, No. 5: 5% $NiO \cdot Co_2O_3$.
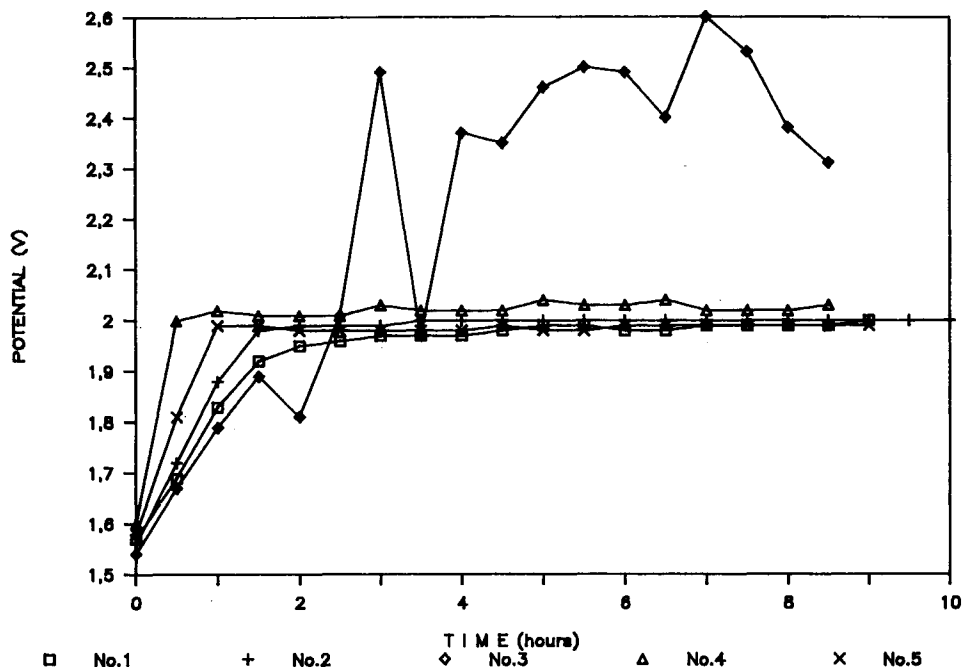
Fig. 5. Potentials of 5% doped electrodes.

The overcharge experiments have been done applying constant current densities between 3 and 10 mA/cm². Parallel experiments with the same type and amount of additive but different current densities showed that variations of the current density in the range from 3–10 mA/cm² had no influence on the results. For comparison in Fig. 4 the results obtained with the higher current densities have been mathematically normalized to 3 mA/cm² and the straight line for the theoretical oxygen evolution was calculated for the same. The voltage/time functions given in Fig. 5 indicate that, besides the irregular performance of zinc cobaltite, a plateau is achieved in all cases situated slightly above the curve of pure MnO_2.

The most promising results of this first series of tests were given by the vanadium oxide (V_2O_5) and by the nickel cobaltite ($NiO \cdot Co_2O_3$) if only the closeness of the cumulative volume of oxygen evolved to the theoretical amount is judged. If the rate of oxygen evolution — after the electrode reached the voltage plateau — is taken into account, $CoO \cdot Al_2O_3$ seems to be equally promising (see Table 1). Consequently, the following experiments should determine if lower concentrations of the doping oxide were able to give similar results. The results for vanadium oxide are summarized in Figs. 6 and 7. The amount of evolved oxygen at a given time is clearly dependent on the concentration of the additive but the effect — as indicated by the identical slope of the curves — is visibly the same. Electrodes doped with less than 1% V_2O_5 might also be satisfactory. The correlation between the concentration of the added oxide and the level of the potential plateau (Fig.

TABLE 1

Activities of additives applied in different concentrations

Experiment no.	Additive	Concentration of additive (%)	Coulombic efficiency[a] (%)
2	$CoO \cdot Al_2O_3$	5	98
6	V_2O_5	5	100
9	V_2O_5	3	98
8	V_2O_5	1	97
7	$NiO \cdot Co_2O_3$	5	100
10	$NiO \cdot Co_2O_3$	3	99
11	$NiO \cdot Co_2O_3$	1	100
14	NiO	1	95
15	Co_3O_4	1	100
17	$NiO \cdot 2CoO$	1	100

[a]For the oxygen evolution reaction after reaching the voltage plateau.
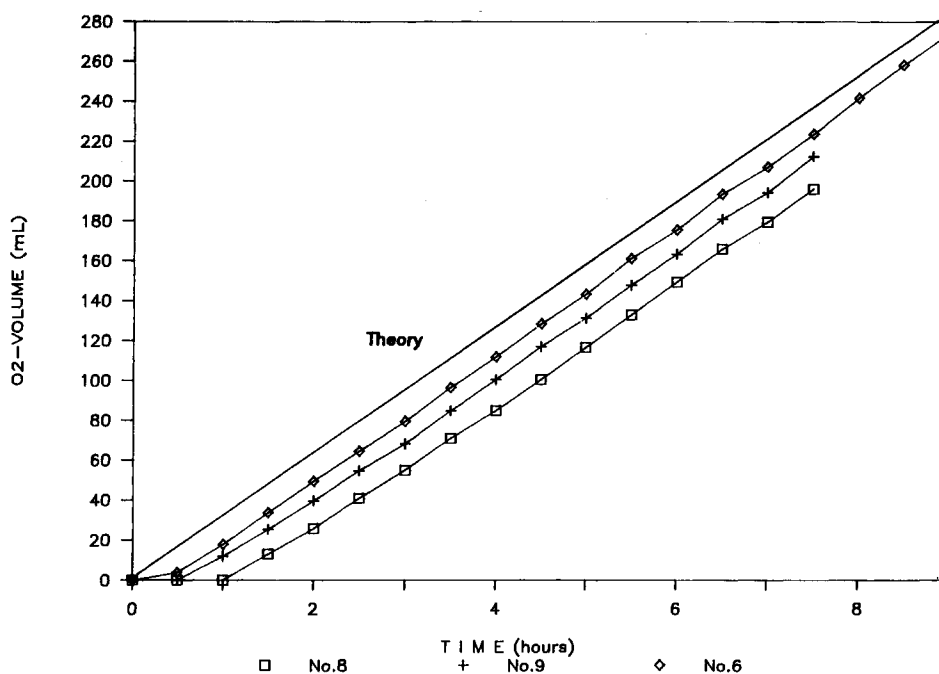
Fig. 6. Oxygen evolution from MnO_2 electrodes. No. 8: 1% V_2O_5, No. 9: 3% V_2O_5, No. 6: 5% V_2O_5.

7) seems to be regular: the higher the amount of vanadium oxide in the electrode the higher the potential in a steady state. In the case of nickel cobaltite the correlation of the results is not so evident. Figure 8 demonstrates that the promotion of the oxygen evolution is nearly not determined by the
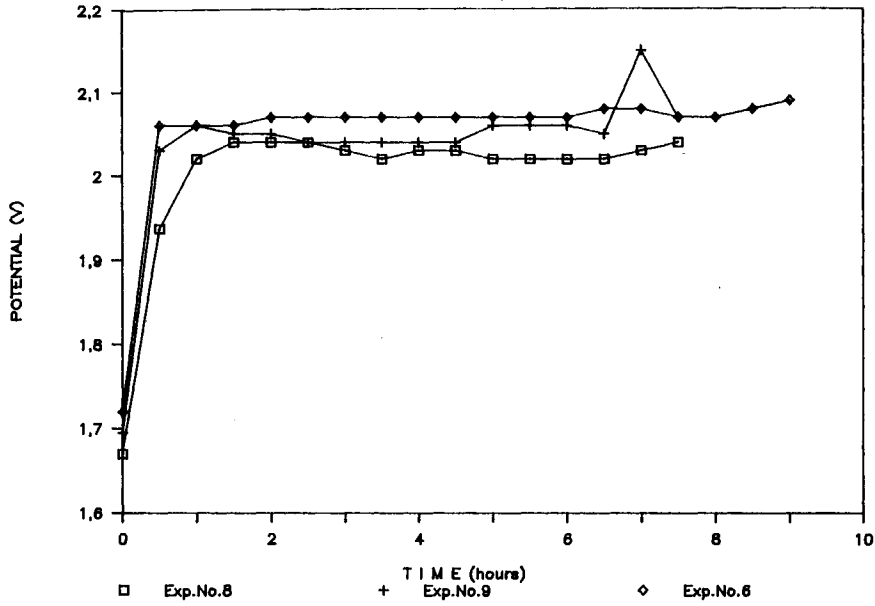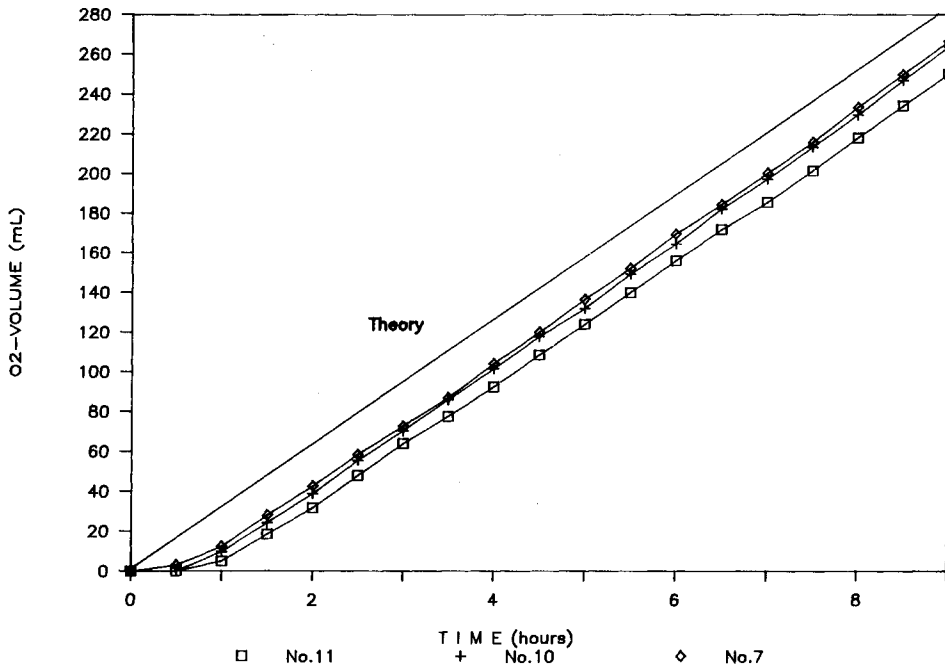
Fig. 7. Potentials of V_2O_5-doped electrodes.

Fig. 8. Oxygen evolution from MnO_2 electrodes. No. 11: 1% $NiO \cdot Co_2O_3$, No. 10: 3% $NiO \cdot Co_2O_3$, No. 7: 5% $NiO \cdot Co_2O_3$.
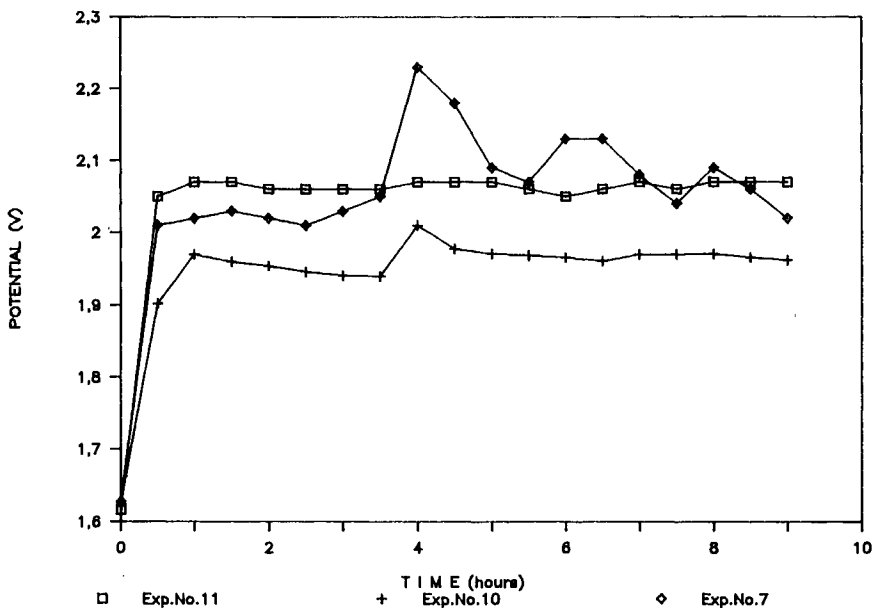

Fig. 9. Potentials of NC-doped electrodes.

amount of additive. 1% of nickel cobaltite gives the same result as 5% and it is possible that even contents below 1% will be active. The potential/time functions reviewed in Fig. 9 point out that there seems to be an optimum at a concentration of 3% which was the least effective from the point of view of oxygen evolution.

Initiated by the results of the X-ray inspection of the used materials it was found necessary to test some additional compounds for their activity in the 1% range. These oxides were NiO, Co_3O_4 and $NiO \cdot 2CoO$. As shown in Fig. 10 the presence of NiO cannot be responsible for the excellent performance of the synthesized nickel cobaltites whereas the activity of the pure cobalt(II)—cobalt(III)—spinel Co_3O_4 is comparable. Another point to be cleared up was the performance of doped electrodes after a period of discharge. For this reason two electrodes containing 5% of nickel cobaltite were prepared and one was discharged for 1 h with a current density of 10 mA/cm^2 and afterwards switched to charge (no. 13, Fig. 11). The other one was discharged for 2 h at 7.5 mA/cm^2 and then reversed at the same current density (no. 12, Fig. 12). The results obtained in both diagrams are compared to adequate experiments with fully charged electrodes. It is apparent that the slope of the curves remains unchanged and only the time-lag before the gassing starts is extended. The recorded potentials show clearly the period of discharge and the subsequent charge (Fig. 13). The higher value for no. 13 is due to the higher current density.
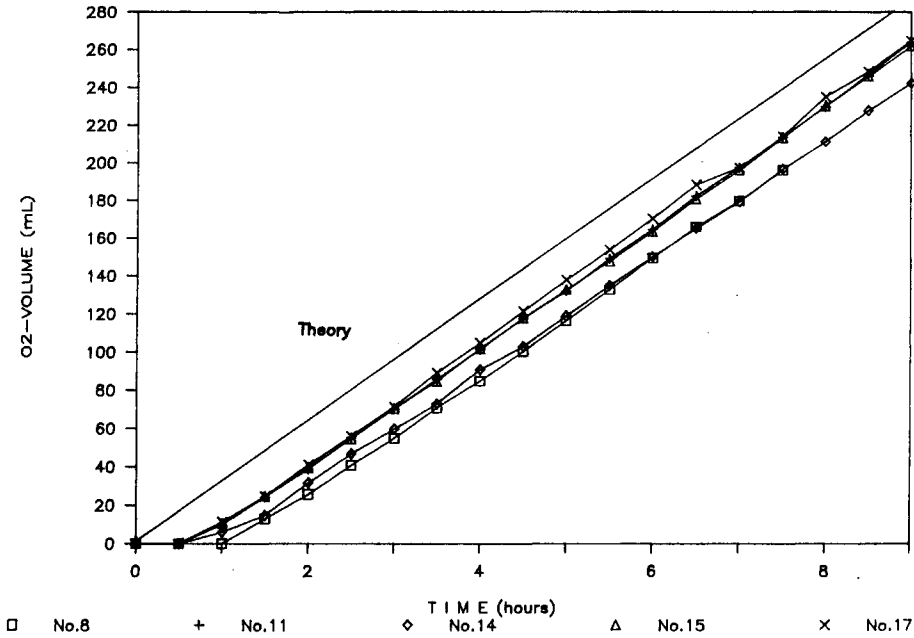
Fig. 10. Oxygen evolution from MnO_2 electrodes. No. 8: 1% V_2O_5, No. 11: 1% $NiO \cdot Co_2O_3$, No. 14: 1% NiO, No. 15: 1% Co_3O_4, No. 17: 1% $NiO \cdot 2CoO$.
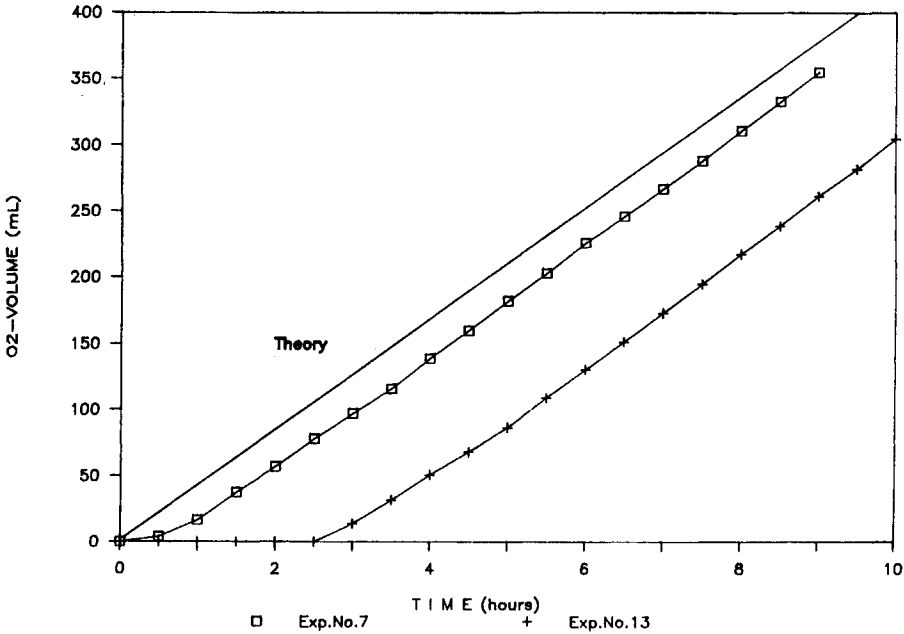

Fig. 11. Oxygen evolution from MnO_2 electrodes. Exp. no. 7: fully charged electrode, 5% NC-doped. Exp. no. 13: 1 h predischarged electrode, 5% NC-doped. Current density: 10 mA/cm^2.
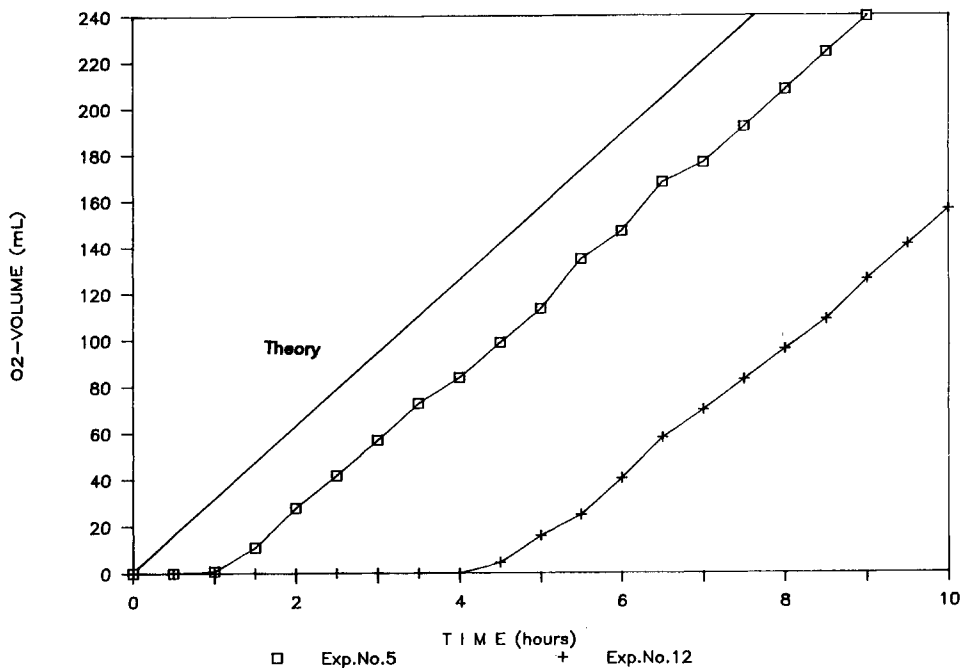
Fig. 12. Oxygen evolution from MnO_2 electrodes. Exp. no. 5: fully charged electrode, 5% NC-doped. Exp. no. 12: 2 h predischarged electrode, 5% NC-doped. Current density: 7.5 mA/cm^2.
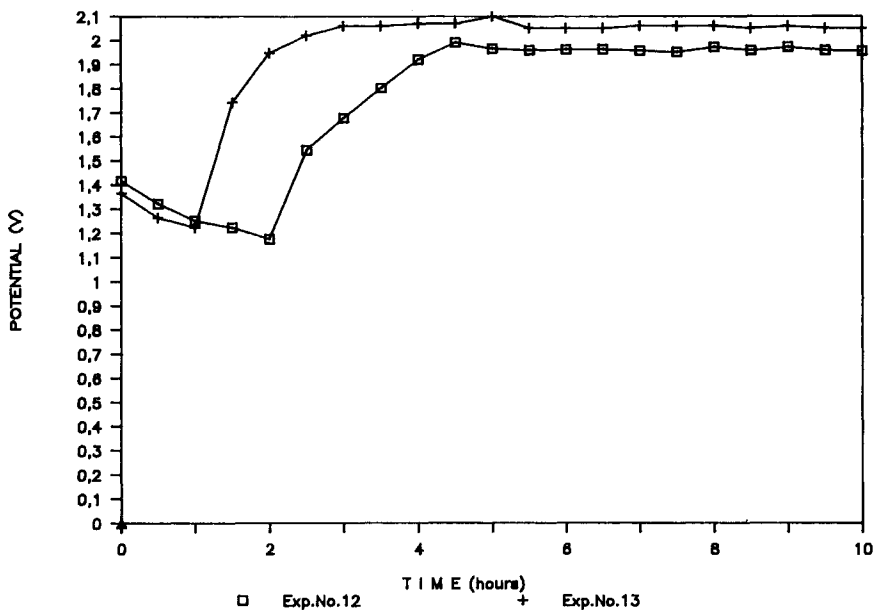

Fig. 13. Potentials of predischarged NC-doped electrodes.

Conclusions

Doping of MnO_2 electrodes with vanadium pentoxide, nickel cobaltites or Co_3O_4 results in a quantitative conversion of input charges to oxygen. The additive is acting without heat treatment of the mixture thus practically excluding the possibility of introducing ions into the MnO_2 lattice. The effect of vanadium pentoxide over a longer period of time seems to be questionable because of its solubility in alkali hydroxides. The nickel cobaltites and the cobalt-spinel are very poorly soluble even in strong acids and bases. Consequently, the addition of these compounds has to be recommended if a certain overcharge protection of MnO_2 electrodes should be provided.

The cited additives are active at currents far higher than those normally observed on cells under overcharge conditions. A constant voltage charger supplies only fractions of a milliampere at the end of charge. Under these circumstances the potential of the electrode is not shifted significantly and the stability of the additive is not a limiting factor.

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