

The effect of alkaline earth titanates on the rechargeability of manganese dioxide in alkaline electrolyte

M. Kloß, D. Rahner*, W. Plieth

Dresden University of Technology, Institute of Physical Chemistry and Electrochemistry, 01062 Dresden, Germany

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Abstract

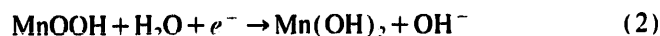
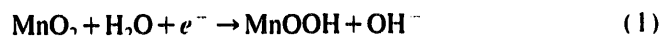
Various alkaline earth titanates were tested as the additives for manganese dioxide electrodes in aqueous electrolyte (9 mol/l KOH) at room temperature. The influence of the additives on the discharge capacity of primary cells and especially on cycling behaviour of rechargeable alkaline batteries is discussed. © 1997 Elsevier Science S.A.

Keywords: Alkaline batteries; Manganese dioxide; Alkaline earth titanate

1. Introduction

Manganese dioxide is one of the most common cathodic battery materials. MnO_2 is inexpensive, non-toxic and readily available. Starting with the Leclanché cell in 1867 the alkaline Zn/ MnO_2 cell is becoming the most used primary battery system. Today, $\gamma\text{-MnO}_2$ becomes an attractive material for rechargeable cells due to economic and ecological reasons.

The discharge mechanism of MnO_2 in alkaline electrolyte is widely investigated [1–3]. The discharge process occurs in two consecutive discharge steps:



The first step, the formation of MnOOH is discussed as a homogeneous solid-phase reaction (Eq. (1)) without changing the basic structure of MnO_2 . During this step, protons are incorporated into the lattice of MnO_2 . This process is accompanied with reduction of Mn^{4+} ions into Mn^{3+} ions within the MnO_2 lattice. The corresponding discharge curve follows more or less the Nernst equation and is characterized by a change in the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio. The discharge reaction is homogeneous and theoretically finished at an oxygen index of $x = 1.5$ in MnO_x .

In addition to this homogeneous reaction the mechanism for the second discharge step is discussed (Eq. (2)). Parts of the initial solid-phase MnOOH are converted via the liquid phase (formation of $[\text{Mn}(\text{OH})_4]^-$ complex ions) into the new solid-phase $\text{Mn}(\text{OH})_2$. The electrochemical process, therefore, consists mostly of the reduction of $[\text{Mn}(\text{OH})_4]^-$ to $[\text{Mn}(\text{OH})_4]^{2-}$ on carbon particles of the conductive additive [1]. This deep-discharge limits strongly the rechargeability of MnO_2 .

For ecological and economic reasons it is desirable to create the alkaline manganese cell as a renewable (rechargeable) system [4,5]. The MnO_2 electrode itself will then encounter a lot of elementary problems with respect to sufficient discharge/charge cycleability.

When discharging of MnO_2 continuously beyond the MnOOH level (second discharge step, Eq. (2)), an irreversible phase transition was observed, and the manganese dioxide lost its fully rechargeability. Bode et al. [6] found, that $\gamma\text{-MnO}_2$ was reduced in a homogeneous phase to $\text{MnO}_{1.6}$ forming an $\alpha\text{-MnOOH}$ (groutite). This means that the $\gamma\text{-MnO}_2$ structure remained unchanged. Bell and Huber [7] described a homogeneous phase reduction to a limit corresponding to $\text{MnO}_{1.7}$.

The depth-of-discharge (DOD) of MnO_2 therefore should be limited to about 0.5 protons per manganese, i.e. $\text{MnO}_{1.75}$, in order to realize MnO_2 with sufficient high cycleability.

In practical, rechargeable Zn/ MnO_2 cells it is recommended to limit the discharge of MnO_2 to a cut-off voltage

* Corresponding author. Fax: +49 (351) 463 71 64; Tel.: +49 (351) 463 43 69.

of 0.9–1.0 V [8]. Another way to control the reduction stage is the limitation of the capacity of the Zn electrode [9].

In addition to these technical possibilities one may observe a variety of attempts in obtaining a sufficient reversible MnO_2 by means of physical and chemical modification of the MnO_2 raw material.

Kordesch and Gsellmann [10] described the formation of $\gamma\text{-MnO}_2$ by means of d.c. electrolysis from acid solutions of divalent manganese(II) ions containing titanyl ions (TiO^{2+}). An electrode, made by this modified MnO_2 , was shown to be rechargeable up to 100 cycles with a DOD of 33% compared with the theoretical one-electron capacity. The reference material (International Common Sample (ICS) No.2) provided only 42 discharge/charge cycles. Kordesch emphasized that a simple mixture of MnO_2 powder and titanium dioxide powder has no positive effect on the rechargeability.

Wroblowa and co-workers [11,12] described the 'activation' of the MnO_2 by bismuth and lead ions. ICS materials and sodium birnessite (NaMn_2O_4) have been modified by means of extensive mechanical mixing with Bi_2O_3 , Bi_2S_3 and PbO , respectively. These doped materials possessed a good cycleability at a reactant utilization within 50–95% of the theoretical two-electron capacity. The practical applicability of these results should be questioned because of the very high excess of the conductive additive.

The influence of bismuth oxide on the electrochemical properties of MnO_2 was also investigated by Axmann and Glemser [13]. They found that the cycleability of the, in general, electrochemically inactive pyrolusite ($\beta\text{-MnO}_2$) could be increased by mechanically grinding with Bi_2O_3 powder. They also proposed a mechanism for the action of the Bi_2O_3 , suggesting a catalytic action. An alternative explanation of the action of Bi_2O_3 is given in Ref. [14]. It was shown, independently of the starting modification of MnO_2 that in the presence of Bi_2O_3 MnO_2 is transformed into a birnessite-like $\delta\text{-MnO}_2$ with a layered structure and that the Bi^{3+} ions are blocking the interconnection points between the layers of MnO_6 octahedrons.

Another way to modify MnO_2 has been reported in Ref. [15]. The described method includes mixing of MnO_2 (γ - or $\beta\text{-MnO}_2$) with an aqueous solution of electrolytes selected from the group consisting of bismuth, lead and copper compounds. Two other methods of chemical modification have been described in Refs. [14,16]. In one method a layered $\delta\text{-MnO}_2$ was prepared by the sol-gel process. A second preparation procedure used a freeze-drying step and a low temperature decomposition producing a spinel structure. Only doped $\delta\text{-MnO}_2$ showed improved cycleability supporting the mechanism presented in Ref. [14]. However, the practical use of these layered MnO_2 as the electrode material is questionable due to the low cell voltage.

Taucher et al. [17] improved the cycleability of alkaline Zn/ MnO_2 cells by means of addition of a barium compound to the cathode mixture. The additives used are barium oxide, barium hydroxide or barium sulfate. It was found that both

the cell capacity and the cumulative capacity increase when the amount of the additive is about 3% of total mass. The mode of additive action is discussed in this way, that the presence of barium compounds in the close vicinity of the cathode material may reduce the access of zinc ions to the MnO_2 , and therefore, the formation of electrochemically inactive hetaerolite ($\text{ZnO}\cdot\text{Mn}_2\text{O}_3$) is substantially lowered. This influence of barium compounds is also described by Bauer [18].

In the work presented here we investigated the discharge behaviour and the rechargeability of MnO_2 electrodes, which contained a physically modified MnO_2 , in an alkaline electrolyte. The 'doped' MnO_2 was produced by physical mixing of MnO_2 powder and an alkaline earth titanate powder.

2. Experimental

A commercial available MnO_2 powder was mixed with an alkaline earth titanate powder (CaTiO_3 , SrTiO_3 or BaTiO_3). The prepared electrodes were combined with a suitable counter electrode (zinc or cadmium) and subjected to the electrochemical measurements.

Both powders, MnO_2 and titanate, were homogenized in the required ratio using a ball mill during at least 8 h. The received product was a physically modified MnO_2 (PM- MnO_2).

The used MnO_2 , also used as pure reference material, was electrolytic manganese dioxide EMD-TRF (Mitsui Co., Japan) with a γ -structure. The EMD-TRF exhibits a theoretical capacity of 308 mAh/g regarding the one-electron step. The positive electrodes were manufactured from a mixture of PM- MnO_2 with a conductive additive (Lonza graphite KS 75). A Teflon suspension or Teflon powder was added as a binder. An aqueous solution of potassium hydroxide (9 mol/l) was used as the alkaline electrolyte at room temperature.

The first experiments were carried out in an electrochemical standard cell with a platinum counter electrode and a Hg/HgO/KOH (9 mol/l) reference electrode (RE). The wet mixture of MnO_2 , conductive additive and binder was pasted onto a nickel mesh with 1 cm² area.

For another series of experiments we combined the MnO_2 electrode with a commercial available zinc or cadmium counter electrode in a button cell, size 2032, see Fig. 1.

For this purpose the mixture of the positive electrode consisted of 40 mg physically modified MnO_2 , 150 mg Lonza graphite KS 75 and 10 mg Teflon powder. This mixture was ground in a mortar and pressed between two nickel meshes into a pellet with a pressure of 30 kN/cm². The obtained electrode pellets were 16 mm in diameter and 1.2 mm in height. The zinc electrode consisted of a porous mercury-free material with a theoretical capacity of 58 mAh/cm². The cadmium electrode (15 mm in diameter) used was 10 times

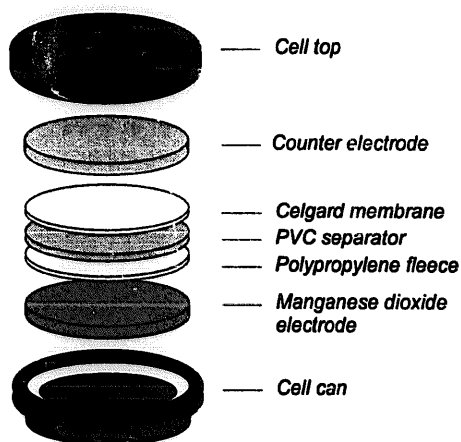


Fig. 1. Scheme of the button cell.

oversized with a theoretical capacity of 130 mAh at an exploitation of 50%.

We used a separator layer system of polypropylene fleece FS 2123WI (Freudenberg, Germany), polyvinyl chloride distance holder and microporous polypropylene membrane Celgard 2500 (Hoechst, Germany).

The electrochemical measurements were carried out by means of an EG&G Princeton Applied Research (PAR) 273A potentiostat/galvanostat controlled by PAR M270 electrochemistry software. A special electronic equipment of MACK Elektronik, Germany, was used for galvanostatic cycleability tests.

3. Results and discussion

The first measurements were performed in electrochemical standard cells using a high excess of alkaline electrolyte.

Fig. 2 shows the cyclic voltammograms of pasted electrodes with unmodified and BaTiO₃-modified MnO₂ in the first cycle. The reduction of the γ -MnO₂ progresses in two steps, indicated by two cathodic peaks. Up to a potential of -0.375 V versus RE the reduction process can be described by Eq. (1). The proton insertion was found to expand the MnO₂ lattice [19]. In the second cathodic peak (potentials lower than -0.375 V) the reduction of Mn²⁺ species occurs according to Eq. (2). In the reverse scan, one observes the anodic step-wise reoxidation of the Mn²⁺ and Mn³⁺ species. The addition of BaTiO₃ leads to a better utilization of MnO₂. Considerably higher specific peak current densities are observed in the cathodic as well as in the anodic scan. The BaTiO₃ additive itself shows no own electrochemical activity within the potential range under investigation.

In the electrochemical standard cell, the discharge/charge behaviour was investigated under galvanostatic conditions.

The electrodes were discharged at a specific current density of 30 mA/g MnO₂ and then charged at the same current density up to a cut-off charge potential of 450 mV versus Hg/HgO/KOH (9 mol/l). The DOD was fixed at 150 mAh/g MnO₂ (this value corresponds to approximately 49% of the theoretical one-electron capacity).

The discharge potentials for the modified and unmodified materials in various cycles are listed in Table 1.

In the case of the BaTiO₃-modified MnO₂ the discharge end potential of -400 mV versus RE is reached only in the 25th cycle. With the undoped MnO₂ this value is measured already in the 10th cycle. The barium titanate additive improves the cycleability of MnO₂ electrodes, but the number of cycles is still very small.

During the investigation of MnO₂ electrodes in model cells various problems arose, therefore not attaining higher cycle numbers. The MnO₂ electrode undergoes a continuously

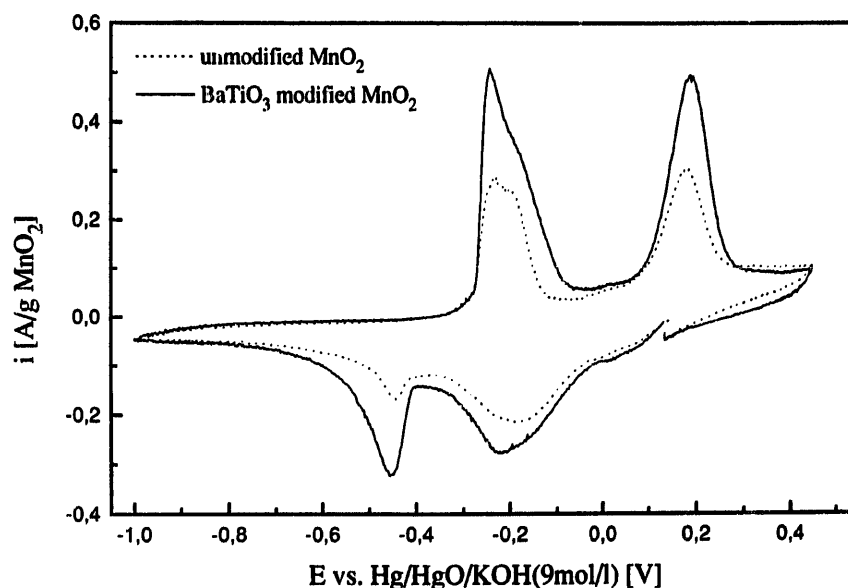


Fig. 2. Cyclic voltammograms for BaTiO₃-modified and unmodified MnO₂ electrodes in the first cycle. Mixture ratio: 95% γ -MnO₂ + 5% BaTiO₃; electrode composition: 20% active material, 75% graphite, and 5% PTFE. Scan rate = 100 μ V/s.

Table 1

End discharge potentials vs. cycle number for modified and unmodified MnO₂; mixture ratio: 95% γ -MnO₂ + 5% BaTiO₃; electrode composition: 47.5% active material, 47.5% graphite, and 5% PTFE. $i = 30$ mA/g MnO₂

Cycle number	BaTiO ₃ -modified MnO ₂ <i>E vs. RE (mV)</i>	unmodified MnO ₂ <i>E vs. RE (mV)</i>
1	-159	-203
5	-277	-310
10	-314	-400
15	-339	
25	-400	

expansion and contraction during cycling tests [20]. Therefore, the resistivity between the graphite and MnO₂ particles increases, depending on the contact of the particles in the pellet.

Another serious problem is the high solubility of manganese(III) ions in the strong alkaline electrolyte [21]. In the oversized electrolyte volume the loss of active material is very important and should not be neglected. The dissolved Mn³⁺ species can be reoxidized and precipitated as MnO₂ particles in the electrolyte. Therefore, the content of the active material in the cathodic mass decreases with time.

In order to diminish these undesired processes we studied the behaviour of our modified MnO₂ samples under practical conditions in button cells with zinc or cadmium counter electrodes. Fig. 3 compares the primary discharge behaviour of the modified MnO₂ samples with the unmodified reference material. The Zn/MnO₂ cells have been discharged with a specific current density of 20 mA/g MnO₂ up to a cell voltage of 0.5 V.

Fig. 3 shows the discharge curves of the Zn/MnO₂ button cells. An addition of alkaline earth titanates to the MnO₂

Table 2

Discharge time of various Zn/MnO₂ button cells, $i = 20$ mA/g MnO₂

	Discharge time up to a cut-off voltage (h)		
	1.0 V	0.9 V	0.8 V
Reference cell	12.7	13.5	14.8
SrTiO ₃ additive	12.8	14.2	17.3
BaTiO ₃ additive	12.7	16.6	17.5

active mass increases the primary discharge capacities of the test cells. The discharge times versus DOD are listed in Table 2.

The results in Table 2 show that the addition of alkaline earth titanates increase the discharge capacity of Zn/MnO₂ primary cells up to 20% (depending on DOD) compared with an unmodified MnO₂ reference cell. These findings are in good agreement with the results of Davis et al. [22].

In order to test the reversibility of the discharge reaction according to Eq. (1) we subjected the button cells to galvanostatic cycling tests.

For the cycling tests the MnO₂ electrode was combined with a cadmium counter electrode. In this way the formation of an electrochemically inactive heterolite (ZnO · Mn₂O₃) was prevented during the measurements.

Consequently, the influence of the examined additives on the cycleability of the MnO₂ electrode could be tested without this undesired side reaction.

Cd/MnO₂ cells were discharged at a specific current density of 100 mA/g MnO₂. The discharge capacity was fixed at 154 mAh/g MnO₂, i.e. 50% of the theoretical one-electron capacity. Charging was carried out with a current density of 50 mA/g MnO₂ until compensation of the discharge capacity. Fig. 4 shows the end voltages of the charge and discharge

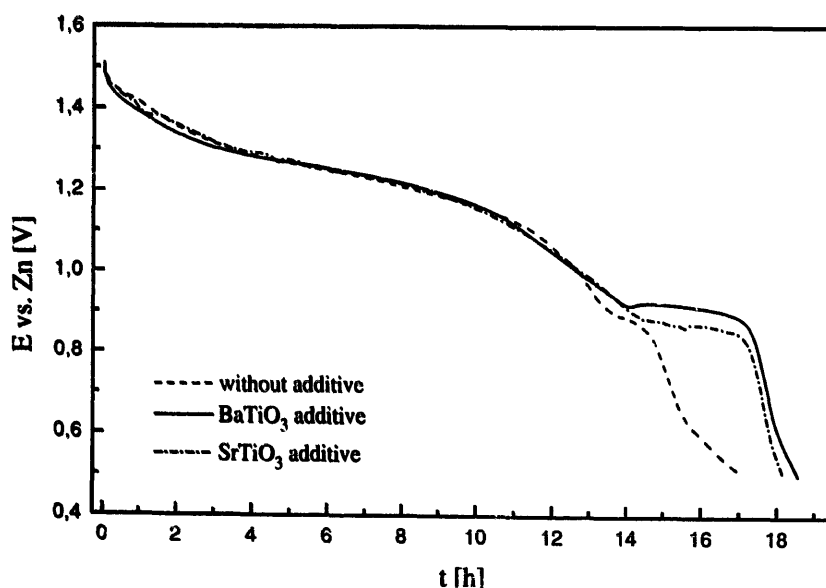


Fig. 3. Constant-current discharge curves of Zn/MnO₂ button cells with modified and unmodified MnO₂; mixture ratio: 75% γ -MnO₂ + 25% titanate, and $i = 20$ mA/g MnO₂.

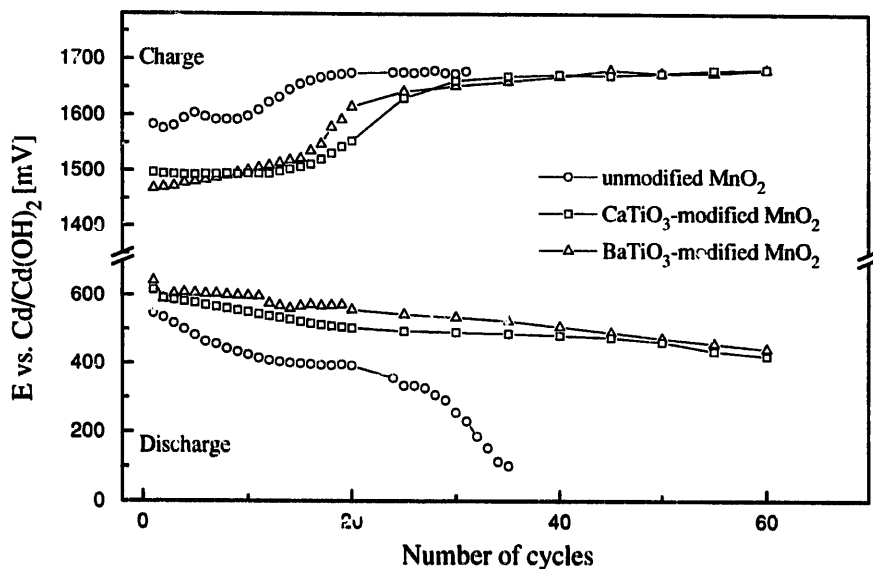


Fig. 4. End voltages of discharge/charge vs. cycle number for modified and unmodified MnO₂ material tested in button cells.

process versus cycle number. The cell containing the unmodified reference material (EMD-TRF) reaches only 36 cycles at a discharge end voltage of 0.1 V. This result is comparable with the experiments of Kordesch et al. [20], who tested various ICS MnO₂ materials with respect to their cycling behaviour.

The cycling characteristics of the modified MnO₂ are better. Cells with the titanate-modified MnO₂ show discharge end voltages higher than 400 mV in the 60th cycle.

In the first charging steps the end voltages of the charging process at the cells with modified MnO₂ are 100 mV lower than the reference cell. In principle the measured charge end voltages are very high. This means that during the charge process side reactions such as oxygen evolution or formation of manganese ions with a valence state higher than four cannot be excluded.

Therefore, we used a modified charging regime with voltage limitation of the charging process to prevent these side reactions. The charging process was divided into a first constant-current step followed by a constant-voltage step (current-voltage charging regime). The complete test regime consisted of:

Discharge $i = 100 \text{ mA/g MnO}_2$, DOD: 50%
 Charge step 1 $i = 50 \text{ mA/g MnO}_2$ up to a cell voltage of 1.4 V
 Charge step 2 $E = 1.4 \text{ V}$ (10 h)

The current and cell voltage versus time during a discharging/charging cycle according to this regime is represented schematically in Fig. 5.

The potential limit of 1.4 V versus Cd/Cd(OH)₂ during charging, which was evaluated by cyclic voltammetric experiments, guarantees prevention of side reactions. The results

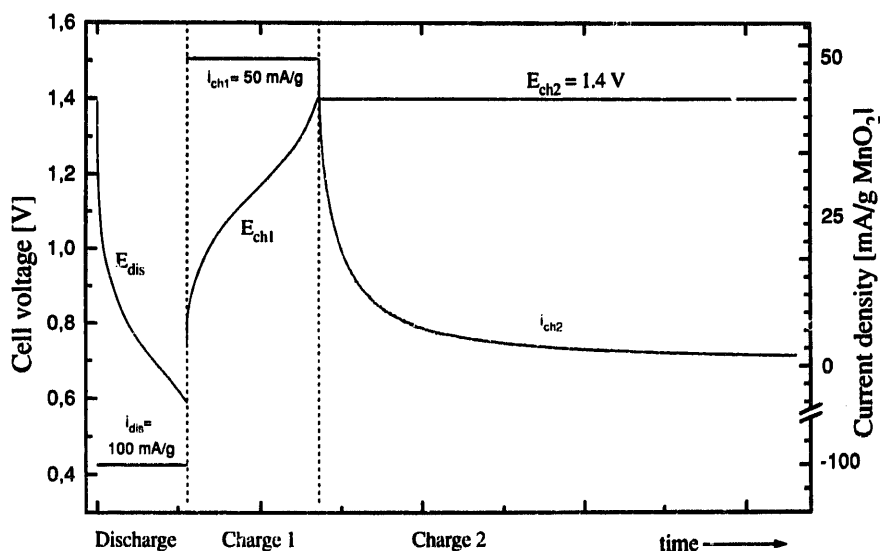


Fig. 5. Scheme of current and cell voltage vs. time during the cycling regime with voltage limitation.

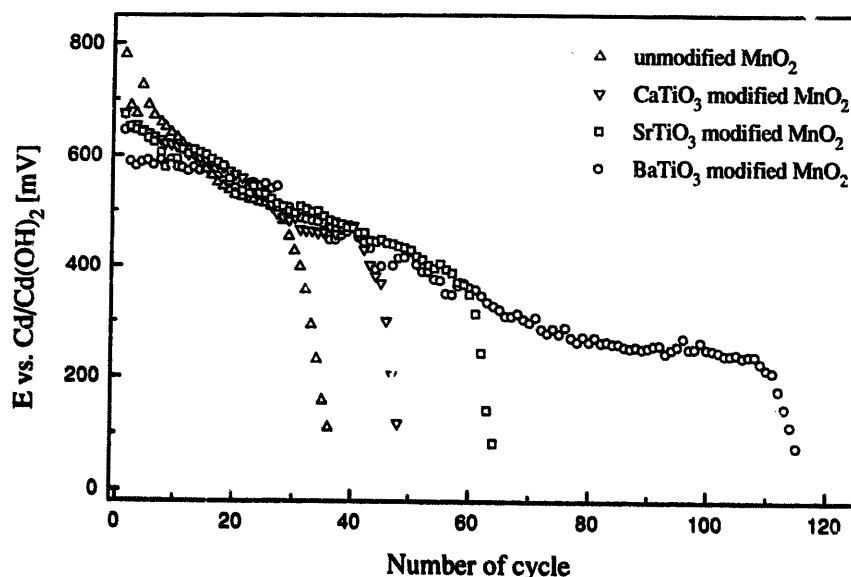


Fig. 6. Discharge end voltages vs. cycle number for modified and unmodified MnO_2 . The button cells were recharged by the current–voltage charging regime.

of the constant-current measurements could be reproduced by this current–voltage charging regime. Fig. 6 shows the discharge behaviour of Cd/MnO_2 button cells using titanate modified MnO_2 electrodes in comparison with a reference cell cycled with the described test regime. In all cases, a charging factor of at least 1.0 could be guaranteed. Therefore, a capacity loss due to incomplete recharging can be excluded.

More than 115 cycles with a DOD of 50% (theoretical one-electron capacity) could be attained with the BaTiO_3 -modified MnO_2 before reaching the chosen discharge limit of 0.1 V. The reference cell (unmodified MnO_2) delivers only 39 cycles under the same conditions. This corresponds to an increase of about 150% in the rechargeability of the MnO_2 electrode compared with the untreated material.

4. Conclusions

The addition of alkaline earth titanates causes a better utilization of MnO_2 during the use in primary batteries. In the presence of these additives the discharge/charge cycleability of MnO_2 is clearly improved.

It is still an open question whether the mechanism of these new additives is similar to Bi_2O_3 . The mechanism of the action of the described additives is under investigation.

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