

Production and characterisation of titanium doped electrolytic manganese dioxide for use in rechargeable alkaline zinc/manganese dioxide batteries

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Abstract

A preliminary screening test of some organo-titanium compounds was conducted. The aim was to find their chemical stability in the electrolyte used for manganese dioxide production. Titanium doped electrolytic manganese dioxide (Ti-EMD) samples were prepared using suitable organo-titanium compounds and a special fine-grained titanium dioxide. The Ti-EMD samples were characterised by conducting physical, chemical and electrochemical tests on them. Physical tests included: X-ray diffraction analysis and BET surface area determination. Chemical test conducted was the determination of titanium content of samples. The electrochemical characterisation involved: cyclic voltammetry, galvanostatic discharge and application of sample in real cell situations. Doped samples performed well in comparison with TOSOH-Hellas GH-S (commercial battery grade electrolytic manganese dioxide). © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The alkaline MnO_2 -Zn cell represents a major advance in portable power sources over most conventional battery types. This battery type is best suited for heavy and continuous drains. Over the years attempts have been made to make manganese dioxide, the cathode material of this battery system rechargeable. Kordesch et al. have made significant progress [1–3]. Through their efforts a practically rechargeable alkaline manganese dioxide (RAMTM) cell was commercialised in 1993.

The present system however, has a limitation to the extent of discharge. In order to achieve rechargeability, only one third of the available theoretical one-electron capacity is permitted on discharge. This conditional depth of discharge is achieved by limiting the cell anodically.

Much attention has been directed at making a new type of rechargeable MnO_2 material for use in this battery

system. Attempts involve introducing dopant ions into the manganese dioxide material employing various methods [4–10]. Hitherto, two kinds of methods were used to introduce the dopants into the MnO_2 :

- (a) Co-precipitation of the MnO_2 material with the dopant. This yields the so-called chemically modified MnO_2 (CM- MnO_2).
- (b) Mechanically mixing the dopant with the MnO_2 material, yielding the physically modified MnO_2 (PM- MnO_2).

The doping materials of major concern in these two techniques are Bi(III)- and Pb(II)-ions. These were co-precipitated [11,12] employing the aqueous solutions containing the required ions thus yielding CM- MnO_2 . Mechanically mixing γ - MnO_2 with Bi_2O_3 or PbO [13] yields PM- MnO_2 .

These ions are known to stabilise the MnO_2 lattice towards dimensional changes that occur during discharging and charging of the material. Though not yet fully understood, they are thought to modify the “open structure” configuration of the MnO_2 material [6–8].

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Electrolytic manganese dioxide is found to be the most suitable MnO_2 material for battery formulation due to its low polarisation.

In recent times, attempts have been made to produce electrolytically doped manganese dioxide for the same reasons as outlined earlier. A potential candidate for this has been Ti(IV)-ion [13]. This is usually done by anodic deposition of EMD from an acidic solution of manganese sulphate containing some Ti(IV)-ions.

In this work, some titanium compounds have been employed in the production of titanium doped electrolytic manganese dioxide (Ti-EMD).

2. Experimental

2.1. Stability test for doping materials

Most titanium compounds available for the doping experiment hydrolyse easily in aqueous solutions. Production of EMD normally employs an acidic solution of MnSO_4 . This part of the work consists of screening some organo-titanium compounds for their ease of hydrolysis in the electrolyte solution. Compounds tested included: Tetra-*n*-propoxytitanium, $\text{Ti}(\text{OC}_3\text{H}_7)_4$; Tetra-*n*-butoxytitanium, $\text{Ti}(\text{OC}_4\text{H}_9)_4$; and Titanium-oxysulphate, $\text{TiO}(\text{SO}_4)$.

2.2. Electrolytic manganese dioxide production

For the production, a laboratory scale electrolyser was built. A four-necked 4-l round bottom flask served as the electrolytic bath. These mouths serve as inlets for a reflux condenser, a thermometer controlled by relay and the electrodes. The electrodes consisted of a three-electrode system made up of one anode and two cathodes. These were separated by spacers made of PVC. The anode was made up of a 9 cm \times 9.5 cm titanium metal sheet while the cathodes of the same dimension were made from lead metal sheets.

For the preparation of materials, 3-l volume of electrolyte solution mixed with 50 ml/l of dopant was introduced into the electrolyser. The electrolyte solution consisted of 112 g/l $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and 98 g/l H_2SO_4 . This was the composition of the electrolytic bath except for the fine-grained TiO_2 doping material, where 0.5 g/l of the material was used.

For all materials, anode current density was maintained at about 6 mA/cm². A cautious current range of 0.98–1.0 A was maintained for the 48-h period of electrolysis. During electrolysis the electrolyser temperature was automatically maintained at 98°C. It was done to permit predominant formation of γ -EMD.

The electrolysis bath was recharged after 24 h. This was done by introducing in small quantities at a time, 40 g of MnCO_3 . The technique replenishes electrolyte with approximate quantity of manganese removed by electrolysis

and provides neutralisation of formed protons. The step is to avoid electrochemical decomposition of EMD deposited at the anode.

At the end of the 48-h period of electrolysis, the electrode system was removed and disassembled. The anode was removed and washed thoroughly with distilled water. The deposited Ti-EMD was mechanically removed and ground with pestle and mortar. The Ti-EMD powder obtained was washed well with 1 mol/l KOH followed by sufficient distilled water until washing solution showed near neutrality at pH 6.5. The Ti-EMD was recovered by filtering under suction and dried at 80°C overnight. The product was sieved using 125- μm mesh screen and stored for characterisation.

2.3. Sample characterisation

Below are the following sample properties which were verified.

2.3.1. Physical properties

2.3.1.1. *X-ray analysis.* X-ray diffraction analysis was carried out on all materials using a Bruker-AXS D5005 Θ/Θ powder diffractometer equipped with a scintillation counter.

2.3.1.2. *Bet surface area determination.* For BET surface area determination, N_2 gas was adsorbed on the Ti-EMD surface with He serving as the carrier gas. The measurement was done with a Quatrochrome instrument.

2.3.2. Chemical properties

The step involved titanium content determination of the products. A spectrophotometric method, which involved the use of standard titanium solutions prepared using 0.1003 g K_2TiF_6 in 10 ml of (1:1) H_2SO_4 solution, was employed. Adsorbance was read at 410 nm.

2.3.3. Electrochemical properties

2.3.3.1. *Cyclic voltammetry.* A new technique of abrasive stripping voltammetry [14], which employs only microgram quantity of material, was used. The potential of the MnO_2 electrode was swept at 2 mV/s using the computer aided IM5d Zahner Electric device. Voltage scanning was started at approximately the open circuit voltage of the material and taken through to +400 mV and –700 mV.

All potentials were measured against Hg/HgO reference electrode with a platinum strip as the auxiliary electrode. The measurement yielded a set of voltage, current and time data for each cycle.

2.3.3.2. *Galvanostatic discharge.* For this determination, MnO_2 electrodes with the following composition were prepared: 80% EMD, 10% Graphite, 10% 9 mol/l KOH

Table 1
Test cell composition

	Material	% Composition
CATHODE	Ti-EMD	84.00
	Graphite (Lonza K44)	8.20
	Acetylene black (I.C. No. 3)	0.40
	9 mol/l KOH	7.40
ANODE	Zinc (type 004F, Union Miniere/B)	61.54
	Zinc oxide (MERCK, reagent grade)	2.01
	Magnesium oxide (MERCK, reagent grade)	0.96
	Starch (FARINEX 267, Avebe)	1.90
	9 mol/l KOH	33.60

Standard cells for comparison used EMD (TOSOH Hellas GH-S) a none doped commercial sample. Open circuit voltage and short circuit current were measured for cells immediately after production. All cells were cycled using a computer-controlled test stand, which uses voltage limiting taper current charging. Cycling conditions are as follows: Load (charging voltage/cell): 1.72 V; Discharge load: 3.9 Ω ; Charging time: 900 min; Cut-off voltage: 900 mV; Intended number of cycles: 40.

The electrodes were pellets made up of 0.5 g quantity of material compressed at 6.37 metric tons per cm^2 using the Carver laboratory press. The pellets were mounted on platinum wire using a special conducting glue (epoxy resin + silver flakes). Acetyl cellulose was used to coat the electrode surface thus preventing electrode disintegration during discharge since expansion occurs in the process.

A nickel mesh served as the auxiliary electrode while the reference electrode was a zinc strip. The galvanostatic discharge was done at 4 mA/g current density using a computer controlled PGZ 301 Voltalab Potentiostat (Radiometer) run by VOLTAMASTER 4 software. Voltage limits for discharge were 1700 mV maximum and 800 mV minimum.

2.3.3.3. Application of materials in real cell situation. The Ti-EMD materials were used in the preparation of the cathode mix of 'AA' size cells with the following battery material compositions (Table 1).

3. Results

3.1. Results of stability tests on dopants

Results are shown in Tables 2 and 3 for certain volumes of dopant + 100 ml of electrolyte + 5 ml (Table 2) and + 10 ml (Table 3) of conc. H_2SO_4 heated at 95°C.

Table 2
Results of various volumes of dopant + 100 ml of electrolyte + 5 ml of conc. H_2SO_4 heated at 95°C

Dopants	Observation	Remarks
5 ml $\text{Ti}(\text{OC}_3\text{H}_7)_4$	Solution turned cloudy before reaching this temperature	Dopant is not stable under this condition
5 ml $\text{Ti}(\text{OC}_4\text{H}_9)_4$	Solution turned cloudy at this temperature	Dopant is not stable under this condition
5 ml $\text{TiO}(\text{SO}_4)$	Solution was slightly cloudy after heating for about one hour	Dopant is quite stable under the condition
10 ml $\text{TiO}(\text{SO}_4)$	Solution turned slightly cloudy at this temperature	Dopant is not of desired stability under this condition

Table 3
Results of dopant + 100 ml of electrolyte + 10 ml of conc. H_2SO_4 heated at 95°C

Dopant	Observation	Remark
5 ml $\text{Ti}(\text{OC}_3\text{H}_7)_4$	Solution cloudy before reaching this temperature	Doping material is not stable
5 ml $\text{Ti}(\text{OC}_4\text{H}_9)_4$	Slightly cloudy	Quite stable
5 ml $\text{TiO}(\text{SO}_4)$	Solution was clear	Very stable

3.2. Results of sample characterisation

3.2.1. Physical and chemical properties

TiO_2 (suspension) doped material (M_1) produced a low BET surface area of 12.73 m^2/g (Tables 4 and 5). Compared with the standard EMD (TOSOH GH-S) material this is quite low. The TiO_2 suspension should be affecting the formation of the micro pores on which the nitrogen gas should have been absorbed at the BET surface area measurement. Ti-EMD (M_2) has a surface area of 56.80 m^2/g and this value is higher than that of the standard EMD (TOSOH GH-S) material. The $\text{TiO}(\text{SO}_4)$ has improved the formation of micro pores on which nitrogen gas was absorbed.

The low yield of Ti-EMD (M_2) should be corresponding to the low current efficiency observed due to the formation of permanganate during the electrolysis. This formation is seen to result from the high acid content of the electrolyte for this particular doping material.

Three main processes may explain the uptake of these impurity ions in the EMD deposition. These are: (a) occlusion, (b) solid-solution formation, (c) adsorption. For a better understanding of the differences that occurred in BET surface area, there is the need to do further work in order to understand the mechanism of incorporation of titanium ions with each doping material.

3.2.2. X-ray diffraction of manganese dioxide samples

The X-ray diffraction patterns of the products Ti-EMD (M_1), Ti-EMD (M_2) and EMD (TOSOH Hellas GH-S, reference) are shown in Fig. 1. All three samples show a characteristic diffraction pattern of $\gamma\text{-MnO}_2$ with diffraction peaks at around 22° ($= 2\theta$). Sharp peaks result from high crystalline materials. Samples of Ti-EMD (M_1) and Ti-EMD (M_2) show sharper peaks than the commercially available reference material.

Table 4
Results on BET surface area and yield of materials

Material	BET surface area (m ² /g)	Yield (% of theory)
Ti-EMD (M ₁)	12.73	84.70
Ti-EMD (M ₂)	56.80	9.79
EMD (TOSOH GH-S)	19.20	–

Ti-EMD (M₁) is the product from TiO₂ suspension, Ti-EMD (M₂) is the product from TiO(SO₄) doping material and EMD (TOSOH GH-S) is none doped commercially available electrolytic manganese dioxide.

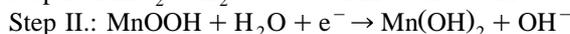
In Fig. 1, the diffraction patterns of Ti-EMD (M₁), Ti-EMD (M₂), and EMD (Tosoh GH-S) have been coupled. This shows that the doped materials function to develop γ -MnO₂ with sufficiently ordered crystalline structure.

It is a known fact that highly crystalline γ -MnO₂ can be obtained at very low current densities [15]. The doping materials should therefore possibly be reducing the true current density at the anode during electrolysis.

3.2.3. Electrochemical properties

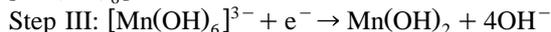
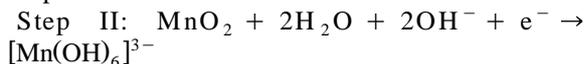
3.2.3.1. *Cyclic voltammetry results*: There are usually two or three cathodic peaks observed in the discharging process. These are:

(A)



(B)

Step I: same as above



(A) Step I is a one-electron homogeneous reduction in solid phase and step II is a one-electron reduction resulting in a differently structured Mn(OH)₂.

(B) Step I is identical to that of reaction path A. After a certain depth of discharge (DOD) it is followed by step II, a heterogeneous one-electron reduction, yielding a soluble Mn(III)-hydroxocomplex. Finally (step III), this complex is reduced to Mn(II) and Mn(OH)₂ is precipitated.

About 30% reduction of γ -MnO₂ occurs in step I and only this reaction remains chemically reversible. Fig. 2a–c are the cyclic voltammograms of the samples: Ti-EMD (M₁), Ti-EMD (M₂) and EMD Tosoh GH-S.

Table 5
Results on the titanium content of materials

Sample	Titanium content (%)
Ti-EMD (M ₁)	1.62
Ti-EMD (M ₂)	4.35

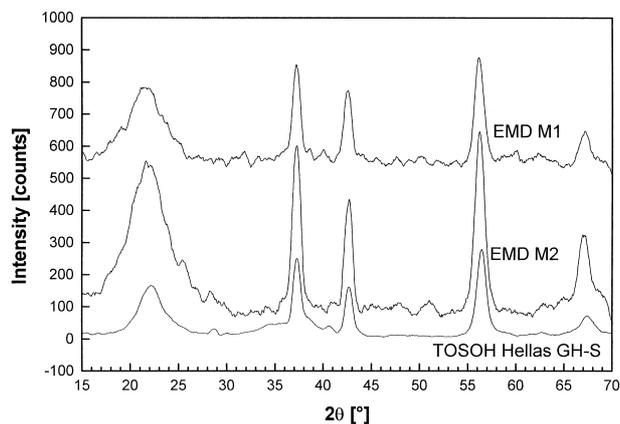
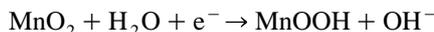
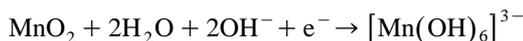


Fig. 1. X-ray diffraction patterns of Ti-EMD (M₁) and Ti-EMD (M₂) compared with that of EMD Tosoh GH-S (Standard).

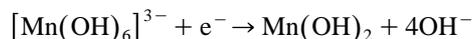
In both doped samples, there is an enhancement of reaction path B in the sequence of discharge reactions:



This reaction will be finished at about -300 mV.



This next step (II) results in a current peak at about -400 mV and the final reduction to Mn(II) (step III)



occurs at about -500 mV.

Similar CV diagrams (potential range -300 to -600 mV vs. Hg/HgO) were obtained by Conway et al. [11] in the course of testing chemically modified (CM) EMDs showing only a very small peak for the homogeneous reduction (step I).

It has to be noticed that the doped samples clearly show three cathodic waves (reaction path B) while the reference (TOSOH Hellas GH-S) shows a wide double peak area in the potential range of step I and only one more peak in the more negative region.

The charging current on the cathodic sweep in all samples occurs at about -250 to $+150$ mV. The highest charge intake with about 1.0 μA peak current is about the same for all the test samples (Table 6).

3.2.3.2. *Results of galvanostatic discharge*. Samples show two distinct regions of discharge corresponding to the homogeneous and heterogeneous reactions as proposed by Kozawa and Yeager [16].

Ti-EMD (M₂) showed the poorest discharge behaviour as can be seen from the discharge time curves (Fig. 3a–c) and the results listed in Table 7.

3.2.3.3. *Results on the application of materials in real battery situations*. Cells with doped material showed higher open circuit voltage than the standard. Standard cells give

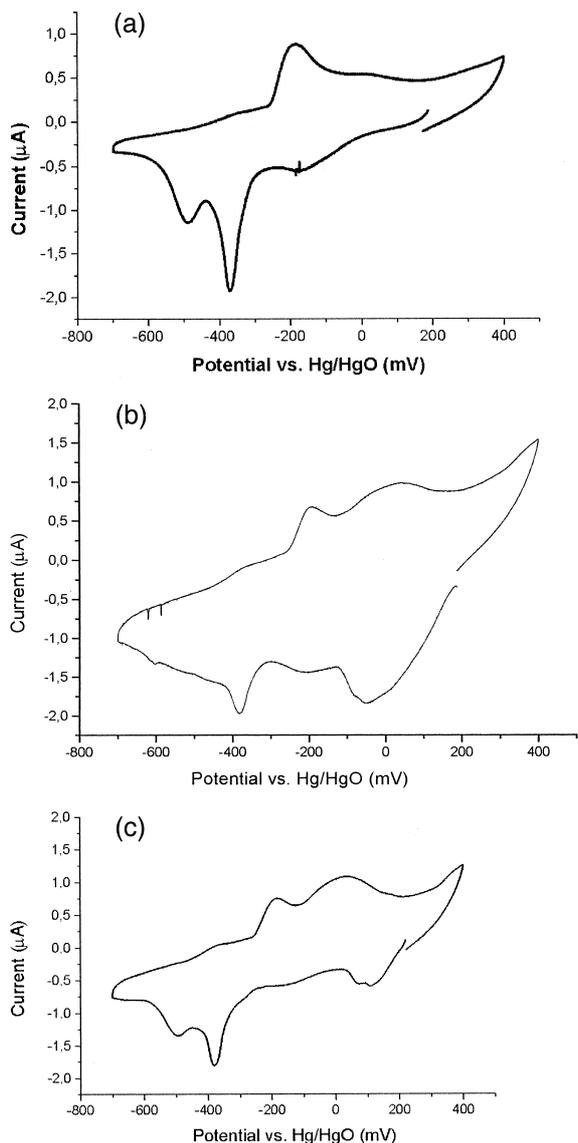


Fig. 2. Cyclic voltammograms for the first cycle of: (a) Ti-EMD (M₁). (b) Ti-EMD (M₂). (c) EMD Tosoh GH-S.

the best short circuit currents. Thus ohmic resistance is least in them. Values from doped material Ti-EMD (M₁) are more encouraging than Ti-EMD (M₂). Cells from this material should be having high internal resistance (Table 8).

The accumulated capacities have been computed from the cycle life performance of the best cell of each material (Fig. 4a–d). Test material Ti-EMD (M₁) showed a better

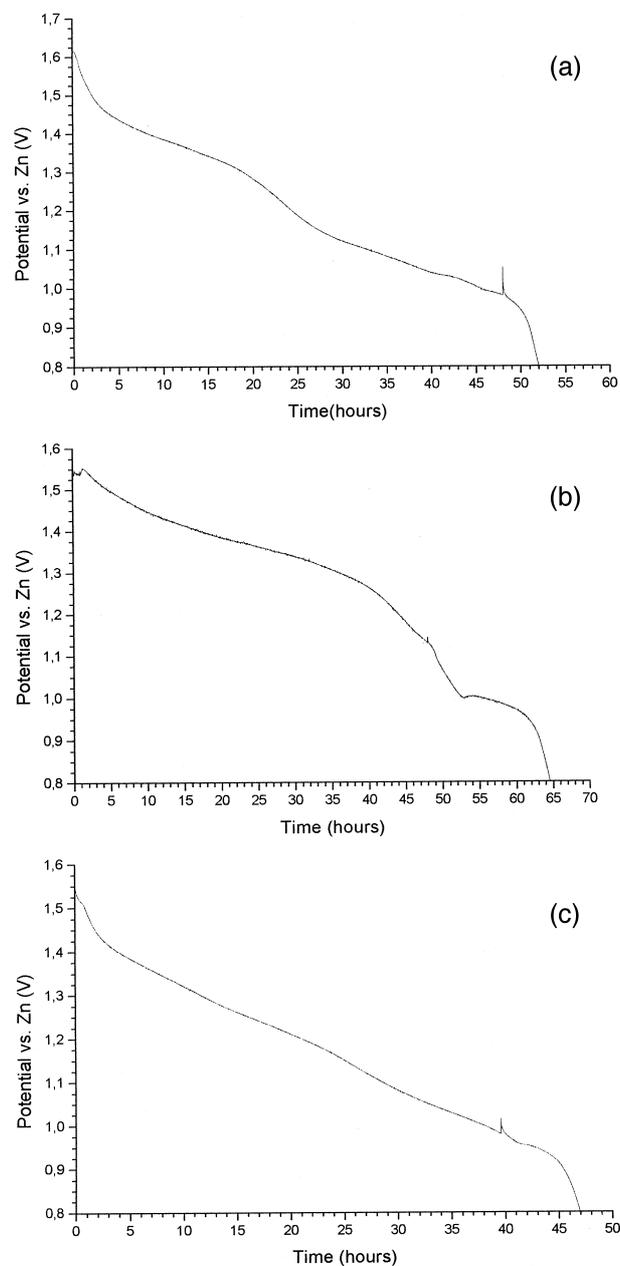


Fig. 3. Galvanostatic discharge for: (a) Ti-EMD (M₁). (b) Ti-EMD (M₂). (c) EMD Tosoh GH-S.

rechargeability than the standard. This is seen in the cell recording a discharge capacity of 449 mA h at the 40th cycle as against the standard with 217 mA h at the same cycle number. Accumulated capacity of this test cell for

Table 6
Reduction peak currents and potentials (voltammograms Fig. 2a–c)

Sample	$-E_{(RI)}$ (mV)	$-E_{(RII)}$ (mV)	$-E_{(RIII)}$ (mV)	$-I_{(RI)}$ (µA)	$-I_{(RII)}$ (µA)	$-I_{(RIII)}$ (µA)
EMD Tosoh	50	380	–	1.75	1.80	–
Ti-EMD (M ₁)	170	380	500	0.60	1.90	1.20
Ti-EMD (M ₂)	–100	380	500	0.60	1.80	1.40

Table 7
Discharge results of pellets described in Section 2.3

Material	Discharge time (h)	Delivered charge (mA h)	Delivered energy (mW h)
Ti-EMD (M_1)	52	83	100
Ti-EMD (M_2)	47	75	88
EMD Tosoh GH-S	65	104	131

Table 8
Cell characteristics immediately after production
VN₁ and VN₂: Standard cells with EMD Tosoh GH-S.
VN₃ and VN₄: Test cells with Ti-EMD(M_1).
VN₅ and VN₆: Test cells with Ti-EMD(M_2).

Cell code	Open circuit voltage (V)	Short circuit current (A)
VN ₁	1.569	7.37
VN ₂	1.576	6.22
VN ₃	1.607	6.05
VN ₄	1.605	6.59
VN ₅	1.617	3.63
VN ₆	1.606	3.23

the 40 cycles is 21.86 A h as against the standard with 21.49 A h. The test cell with Ti-EMD (M_2) has performed poorly under real cell conditions. The discharge capacity

started at a value of 847 mA h for the first cycle and ended at 94 mA h at the 40th cycle. This is not too surprising, bearing in mind the low short circuit current recorded for the cell earlier.

4. Conclusion

Increased acid content of electrolyte bath stabilises the doping material but is detrimental to doped EMD production. The Mn^{2+} electrolyte is being converted to MnO_4^- due to the high acid concentration during electrolysis. This conversion gives rise to low yield of product as it occurred in Ti-EMD (M_2). There is the need for further work to find the critical acid concentration, which will optimize both stability and product yield.

Titanium doping of electrolytic manganese dioxide enhances cycle life performance of the alkaline manganese dioxide cell. This is evident from the higher capacity at the 40th cycle of test cell prepared from Ti-EMD (M_1) as against the output for the standard cell at the same cycle number. However, the performance of the doped material seems to be dependent upon the nature of the dopant. One would have thought the higher surface area and titanium

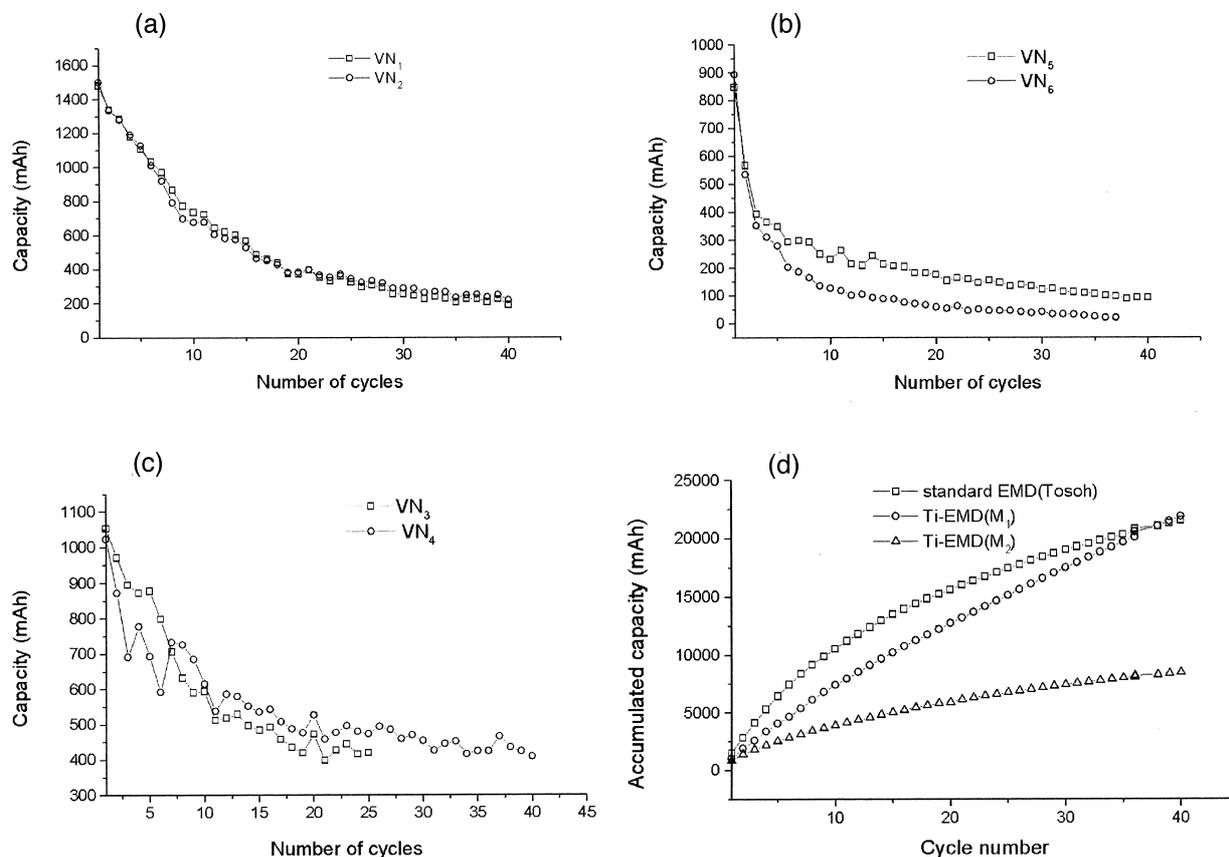


Fig. 4. Cycle life performance of: (a) standard cells with EMD Tosoh GH-S. (b) test cells with Ti-EMD (M_1). (c) test cells with Ti-EMD (M_2). (d) Accumulated capacity of cells versus cycle number.

content of Ti-EMD (M_2) would greatly enhance its performance. The test cell from this material performed quite poorly.

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