

# Studies on electrochemical performance of partially reduced $\text{MnO}_2$ used as cathode for MH– $\text{MnO}_2$ rechargeable battery

Xi Xia<sup>a</sup>, Chunxia Zhang<sup>a</sup>, Zaiping Guo<sup>b,\*</sup>, H.K. Liu<sup>b</sup>, Geoff Walter<sup>b</sup>

<sup>a</sup>*Institute of Applied Chemistry, Xinjiang University, Xinjiang, PR China*

<sup>b</sup>*Institute for Superconducting and Electronic Materials, University of Wollongong, NSW 2522, Wollongong, Australia*

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## Abstract

Cyclic voltammograms show that the reversibility of the manganese dioxide ( $\text{MnO}_2$ ) electrode is improved by means of using partially reduced samples. The crystal lattice of the intermediate is transformed by reduction. Formation of the manganese ion is very limited before the electrode potential reaches  $-0.4$  V (versus Hg/HgO), thus the formation of  $\text{Mn}_3\text{O}_4$  is prevented.

The addition of  $\text{Ni}(\text{OH})_2$  to partially reduced samples can further improve the reversibility of the  $\text{MnO}_2$  electrode,  $\text{Ni}(\text{OH})_2$  delays the  $2e^-$  discharge step and decreases the opportunity for the co-existence of Mn(III) and Mn(II) ions and, thereby, prevents the formation of  $\text{Mn}_3\text{O}_4$ . The capacity retention of a cathode of partially reduced  $\text{MnO}_2$  (pr- $\text{MnO}_2$ ) or pr- $\text{MnO}_2 + \text{Ni}(\text{OH})_2$  is much better than that of the  $\text{MnO}_2$  cathode. This demonstrates the feasibility of using pr- $\text{MnO}_2$  as a cathode material. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Battery partial reduction; Manganese dioxide; Cyclic voltammetry; Nickel hydroxide

## 1. Introduction

The metal-hydride–manganese dioxide (MH– $\text{MnO}_2$ ) secondary battery has some advantages, such as long-cycle life, non-toxicity, low self-discharge rate, high performance/cost ratio and non-memory effect [1], although it is a prospective and novel rechargeable battery. In past years, progress in our research on MH– $\text{MnO}_2$  secondary batteries has been made. Now, the life of 3.5 Ah prismatic MH– $\text{MnO}_2$  battery has been raised to over 1400 cycles, while that of AAA cylindrical MH– $\text{MnO}_2$  batteries has been increased to over 450 cycles and the capacity to above 450 mAh [2]. We consider that properties of MH– $\text{MnO}_2$  secondary batteries can also be improved, but this requires an enhancement in the performance of the  $\text{MnO}_2$  cathode.

The basic obstacle in advancing of MH– $\text{MnO}_2$  batteries is that the initial charge and discharge states of the cathode and anode are mismatched, i.e. the  $\text{MnO}_2$  is in the charged state, but MH is in the discharged state [3]. In past years, we have investigated many methods to overcome this problem, such as adding an appropriate amount of the discharged state material,  $\text{Ni}(\text{OH})_2$ , to the  $\text{MnO}_2$  cathode to moderate the mismatch. We have also used a special, seven-step,

multi-cycle formation method to make the cathode and anode match gradually [4]. The process of formation is too complex, however, and is too equipment dependent. Also, overcharging of the  $\text{MnO}_2$  cathode cannot be avoided completely, i.e. small amounts of  $\text{MnO}_2$  are overcharged and some Mn(VI) is formed. Therefore, capacity of the  $\text{MnO}_2$  is irreversibly lost. To completely avoid the mismatch of the initial charge and discharge states of cathode and anode, we have chosen to use pr- $\text{MnO}_2$  as the cathode material for the MH– $\text{MnO}_2$  battery. Qu [5] has discussed the feasibility of using MnO and MH as production materials for the MnO–MH battery. It was reported that the MnO–MH working voltage was below 1 V, which restricts its application as a single cell, but the system could possibly be used in battery packs or in a bipolar configuration.

We consider that MnO is not suitable as a cathode material because  $\text{Mn}^{2+}$  cannot be oxidized to  $\text{MnO}_2$  completely during the charging process, and the  $\delta\text{-MnO}_2$  produced is easily reduced to  $\text{Mn}_3\text{O}_4$ , which leads to massive capacity loss [6]. Therefore, we have used pr- $\text{MnO}_2$  instead of MnO. In order to raise the working voltage and improve the performance of the cathode, it is still necessary to add  $\text{Ni}(\text{OH})_2$  to the  $\text{MnO}_2$  cathode. Based on the results obtained, it is obvious that the reversibility of the  $\text{MnO}_2$  electrode can be improved by using pr- $\text{MnO}_2$  as initial active material. The pr- $\text{MnO}_2$  could be promising active material for a  $\text{MnO}_2$  secondary battery.

\* Corresponding author. Tel.: +61-2-4221-3017; fax: +61-2-4221-5731.  
E-mail address: zg04@uow.edu.au (Z. Guo).

## 2. Experimental

### 2.1. Preparation of partly reduced $MnO_2$

$MnO_2$  powder (4.35 g IC No. 1) was suspended in distilled water (20 ml) contained in a 100 ml conical flask together with a small magnetic rod. Three such flasks were prepared, with 0.5, 1.0 or 1.5 ml hydrazine hydrate (AR) added to the moderately stirred suspensions, respectively. Each sample was stirred for 30 min, then filtered and rinsed. The powders were dried at 40 °C in air. Three samples with different degrees of reduction were thus obtained.

### 2.2. Chemical analysis and X-ray diffraction

The degree of reduction was determined by  $FeSO_4$  using a potentiometric titration procedure [7] and found to be  $MnO_x$ , where  $x$  equals 1.78, 1.67 and 1.56, respectively. The crystal structure of the samples was characterized by powder X-ray diffraction (XRD) using a MIC M18-XCE diffractometer with  $Cu K\alpha$  radiation.

### 2.3. Electrochemical measurements

The working electrode contained 20 mg active material, 20 mg graphite, and 10 mg acetylene black. A platinum wire was used as a counter electrode and  $Hg/HgO$  was used as a reference electrode. The electrolyte was aqueous 6 M  $KOH + 15 g l^{-1} LiOH$ . The following three types of powders were used as active materials:  $MnO_x$ ,  $MnO_2$  and  $MnO_x + Ni(OH)_2$  (5:1). Cyclic voltammetry measurements were carried out by means of CHI660 electrochemistry workstation, with a scan rate of  $2 mV s^{-1}$ . A charge–discharge test was carried out with an Arbin BT2024 cell test instrument.

### 2.4. Potentiostatic test

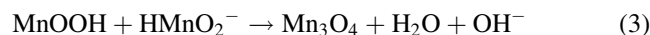
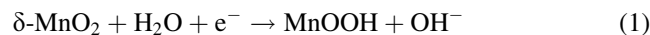
The samples contained 80 mg  $MnO_{1.78}$  (or 66.7 mg  $MnO_{1.78} + 13.3 mg Ni(OH)_2$ ), 40 mg graphite and 10 mg acetylene black. The tests were carried out after each charge–discharge cycle by using a CHI660 electrochemistry workstation. A potential step ( $\Delta E = 15 mV$ ) was applied to the electrodes after each discharge cycle. The current passing between the counter and working electrodes was measured as a function of time after the potential step ( $I-t$  curves). Using current–time plots, the proton diffusion coefficient ( $D$ ) and the variation of  $D$  with cycle number were estimated.

## 3. Results and discussion

### 3.1. Comparison of cyclic voltammograms of partly reduced samples of $MnO_2$

The cyclic voltammogram for IC No. 1  $MnO_2$  and for a partly reduced sample  $MnO_{1.78}$  is shown in Fig. 1a and b,

respectively. It is evident that the voltammograms are different. A broad cathodic peak appears in Fig. 1a over the range  $-0.2$  to  $-0.5 V$  on the first cycle, which corresponds to the reactions  $MnO_2 \rightarrow MnOOH$ ,  $MnOOH \rightarrow Mn(OH)_2$ , and the formation of  $Mn_3O_4$ . The peak is divided into two at  $-0.22$  and  $-0.4 V$  on the second cycle. The peak areas for the reaction  $MnOOH \rightarrow Mn(OH)_2$  and the formation of  $Mn_3O_4$  are larger than the peak area of the first reduction at  $-0.22 V$  [6]. The peak current decreases with cycling. There is only one oxidation peak at  $-0.1 V$ , which corresponds to the reaction  $Mn(OH)_2 \rightarrow \delta-MnO_2$  [8]. The area of the oxidation peak is smaller than that of reduction peak. This shows that reversibility of the electrode is poor, the main reason being the formation and accumulation of inactive  $Mn_3O_4$ . McBreen [6] studied  $\beta$ - and  $\gamma$ - $MnO_2$  in alkaline electrolyte, and concluded that the overall electrode reaction process was as follows. When  $\delta-MnO_2$  was reduced, not only  $MnOOH$  was formed, but also  $Mn(II)$  could be produced as  $HMnO_2^-$ . The reaction sequence is:



There is a peak at  $-0.2 V$  for reaction (1) and another peak at  $-0.4 V$  for reactions (1) and (2), see Fig. 1. The voltammogram for  $MnO_{1.78}$  (Fig. 1b) shows that there is only a couple of oxidation/reduction peaks in the first three cycles. The reduction peak at  $-0.24 V$  can be attributed to the homogeneous phase reaction of  $Mn(IV) \rightarrow Mn(III)$ , while oxidation peak at  $-0.1 V$  is due to the formation of  $\delta-MnO_2$ . The peak current increases rapidly with cycling. A weak reduction peak appears at  $-0.4 V$  on the fourth cycle. This corresponds to the formation of  $Mn(OH)_2$  and  $Mn_3O_4$ . Compared with the behavior of  $MnO_2$  (Fig. 1a), the reduction peak of  $MnO_{1.78}$  at  $-0.4 V$  appears slowly and weakly, so the reversibility of the electrode is improved.

### 3.2. Analysis of cyclic voltammograms of samples with different degrees of reduction

Cyclic voltammograms for samples  $MnO_{1.78}$ ,  $MnO_{1.67}$  and  $MnO_{1.56}$  are presented in Fig. 1b and c, respectively. It is seen that the voltammograms for  $MnO_{1.78}$  and  $MnO_{1.67}$  are very similar. Strong peaks appear at  $-0.24 V$  and correspond to the homogeneous phase reaction of  $Mn(IV) \rightarrow Mn(III)$  [6]. The peaks at  $-0.37$  and  $-0.34 V$  in both curves are attributed to the formation of  $Mn_3O_4$  and the heterogeneous phase reaction of  $\delta-MnO_2 \rightarrow Mn(OH)_2$ . Moreover, the peak current of the two samples increases rapidly with cycling. The cyclic voltammograms of  $MnO_{1.56}$  (Fig. 1d) are different from those for  $MnO_{1.78}$  and  $MnO_{1.67}$ . Two reduction peaks at  $-0.24$  and  $-0.6 V$  appear on the first cycle and result from the reactions of  $MnO_2 \rightarrow MnOOH$  and  $MnOOH \rightarrow Mn(OH)_2$ . A strong peak for the formation of  $Mn_3O_4$  at  $-0.38 V$  appears on subsequent cycles. The peak

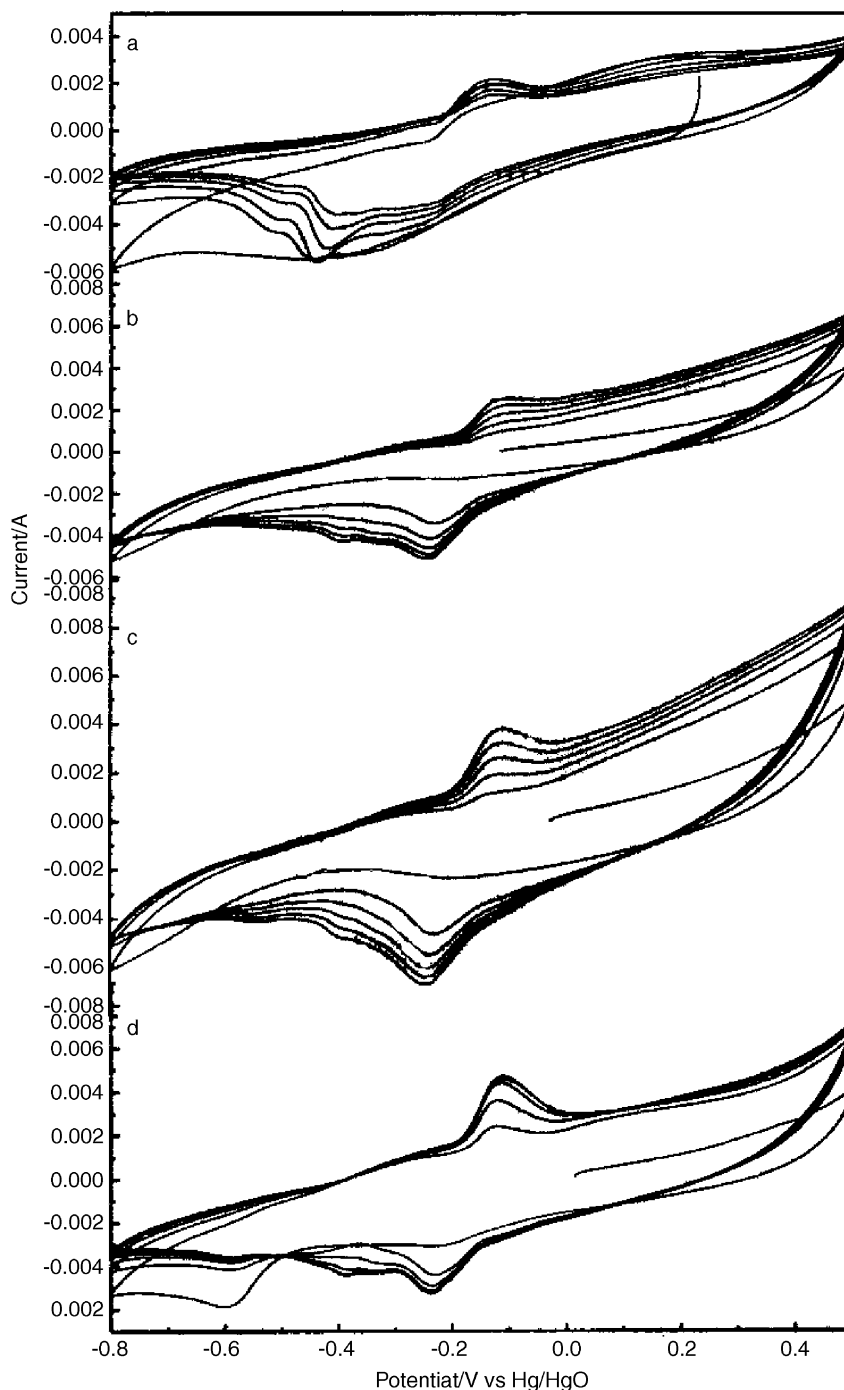


Fig. 1. Cyclic voltammograms of (a) IC No. 1  $\text{MnO}_2$ ; (b)  $\text{MnO}_{1.78}$ ; (c)  $\text{MnO}_{1.67}$ ; (d)  $\text{MnO}_{1.56}$ .

at  $-0.6$  V, corresponding to  $\text{MnOOH} \rightarrow \text{Mn}(\text{OH})_2$ , decreases rapidly with subsequent cycles. This is the result of the formation of  $\text{Mn}_3\text{O}_4$  which consumes part of the  $\text{MnOOH}$ .

The XRD patterns of the different pr- $\text{MnO}_2$  samples are compared in Fig. 2. The differences are caused by different degrees of reduction. The degree of reduction of  $\text{MnO}_{1.56}$  is so high that the crystal lattice of  $\text{MnO}_2$  is cracked and  $\text{Mn}_3\text{O}_4$  forms more rapidly. It can be inferred that the partial reduction of  $\text{MnO}_2$  should be controlled in the range where the crystal lattice of  $\text{MnO}_2$  is not cracked.

There is much controversy about the limit of crystal lattice cracks for  $\text{MnO}_2$ . Some researchers think it is  $\text{MnO}_{1.75}$ , but others believe that it should be  $\text{MnO}_{1.60}$  or  $\text{MnO}_{1.50}$  [9–12]. Maskell et al. [13] studied the chemical and electrochemical reduction of  $\text{MnO}_2$  by means of XRD techniques and considered that electrons which entered the lattice were non-localized in two adjacent Mn(IV) ions between  $\text{MnO}_{1.75}$  and  $\text{MnO}_2$ , but localized between  $\text{MnO}_{1.75}$  and  $\text{MnO}_{1.5}$ , and every electron interacts with a Mn(IV) cation to form an Mn(III) ion. These experiments indicate that, for

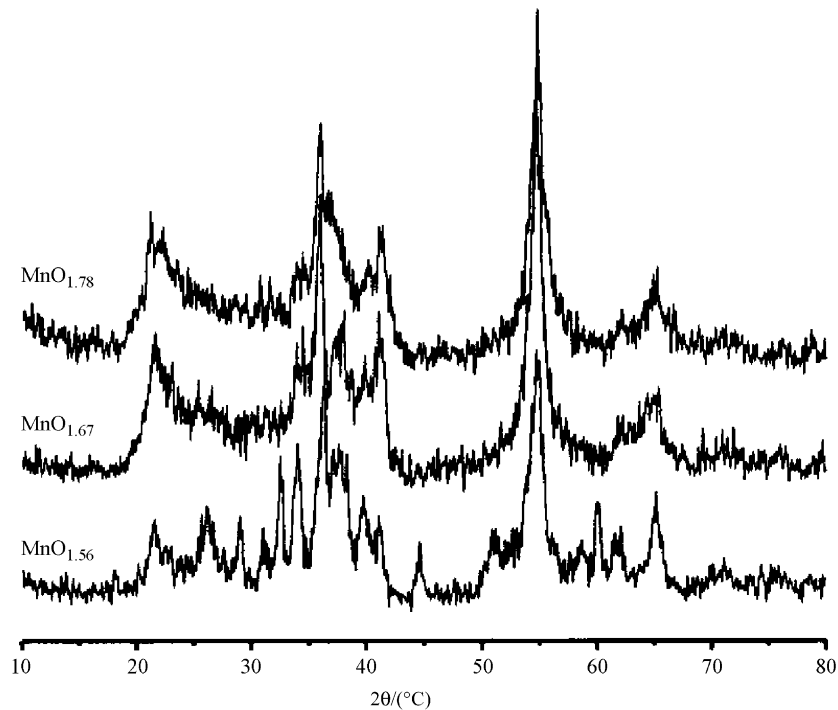


Fig. 2. XRD patterns for (a)  $\text{MnO}_{1.56}$ ; (b)  $\text{MnO}_{1.67}$ ; (c)  $\text{MnO}_{1.78}$ .

different crystal lattices of  $\text{MnO}_2$ , the reduction reactions from  $\text{MnO}_2$  to  $\text{MnO}_{1.5}$  are different. Fernerds et al. [14] reported that the reduction of  $\beta\text{-MnO}_2$  was a homogeneous phase reaction in a very narrow region (from  $\text{MnO}_2$  to  $\text{MnO}_{1.96}$ ). On the other hand, Bell and Huber [10] concluded that the homogeneous phase reduction reaction was probably from  $\text{MnO}_{1.8}$  to  $\text{MnO}_{1.6}$ . Kazawa and Powers [11] studied  $\gamma\text{-MnO}_2$  prepared by heat treatment and proposed that the reaction from  $\text{MnO}_2$  to  $\text{MnO}_{1.5}$  involved a homogeneous phase reduction. Fernerds [14] suggested that homogeneous phase reduction of  $\alpha\text{-MnO}_2$  could only occur until the degree of reduction reached  $\text{MnO}_{1.82}$ , and

the homogeneous reaction increased with increase of the  $\gamma\text{-MnO}_2$  microstructure in  $\alpha\text{-MnO}_2$ . From the results of reported here, we conclude that the limit of crystal lattice cracking is  $\text{MnO}_{1.60}$  in the reduction reaction for  $\gamma\text{-MnO}_2$ .

### 3.3. Influence of $\text{Ni}(\text{OH})_2$ as additive

A cyclic voltammogram for  $\text{MnO}_{1.67}$  with small additions of  $\text{Ni}(\text{OH})_2$  is shown in Fig. 3. Compared with the voltammogram for  $\text{MnO}_{1.67}$  alone (Fig. 1c), the peak currents of the electrode with  $\text{Ni}(\text{OH})_2$  are increased. Three reduction peaks appear at 0.25,  $-0.24$  and  $-0.4$  V, while only one oxidation

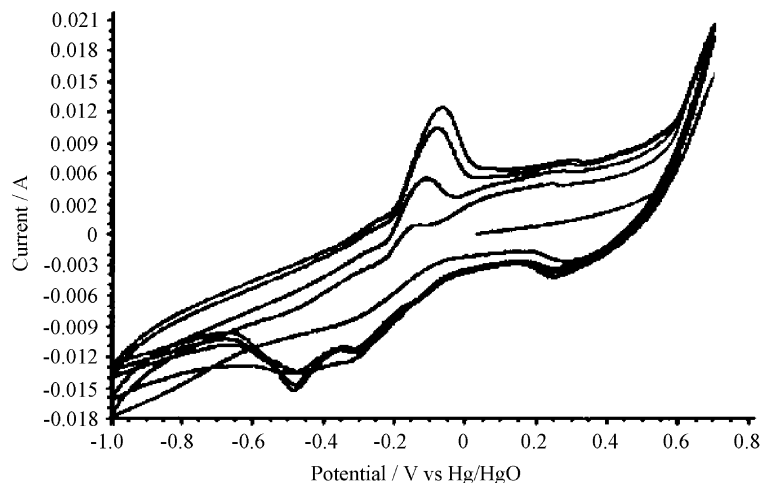


Fig. 3. Cyclic voltammogram of  $\text{MnO}_{1.67}$  with added  $\text{Ni}(\text{OH})_2$ .

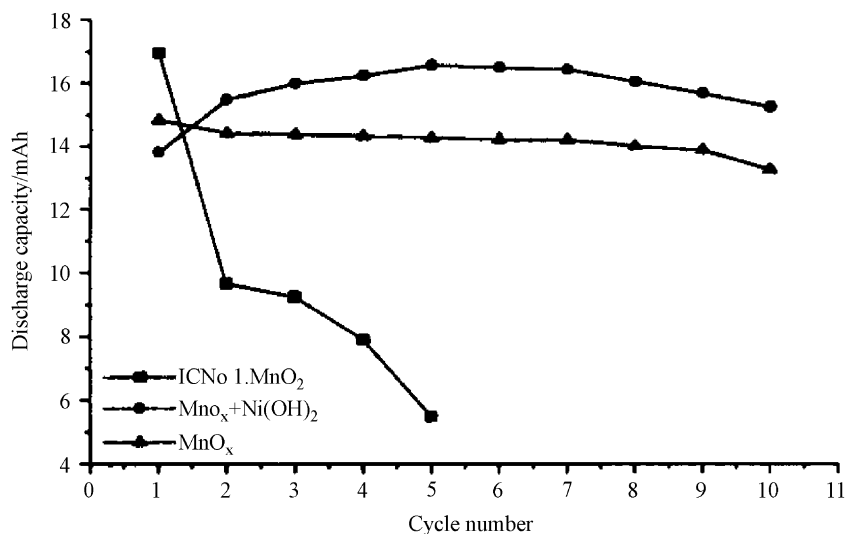


Fig. 4. Variation of discharge capacity with cycle number for given batteries.

peak is present at  $\sim -0.1$  V. These four peaks correspond to the reduction of  $\text{NiOOH} \rightarrow \text{Ni(OH)}_2$ ,  $\text{Mn(IV)} \rightarrow \text{Mn(III)}$ ,  $\text{Mn(III)} \rightarrow \text{Mn(II)}$  and the oxidation of  $\text{Mn(II)} \rightarrow \delta\text{-MnO}_2$ , respectively. The oxidation peaks for  $\text{Ni(OH)}_2 \rightarrow \text{NiOOH}$  do not appear. This is probably because the scanning rate is so fast that evolution of oxygen begins at 0.55 V. The area of the oxidation peak at  $-0.1$  V is roughly the same as the total area of reduction peaks at  $-0.24$  and  $-0.4$  V, which suggests that the reversibility of  $\text{MnO}_2$  is improved. This is mainly because the formation peak for  $\text{Mn}_3\text{O}_4$  does not appear at  $-0.4$  V. Therefore, it can be concluded that the addition of  $\text{Ni(OH)}_2$  further prevents the formation of  $\text{Mn}_3\text{O}_4$ .

### 3.4. Results and discussion of charge–discharge tests

The results of charge–discharge tests are presented in Fig. 4. As far as IC No. 1  $\text{MnO}_2$  is concerned, the discharge capacity on the second cycle is 51% of that on the first cycle. For the partly reduced sample, however, the discharge capacity on the fifth and tenth cycle is 90 and 89% of that on the first cycle, respectively. For the pr- $\text{MnO}_2$  sample with additions of  $\text{Ni(OH)}_2$ , the capacity reaches a maximum at the fifth cycle, and the discharge capacity on the tenth cycle is 92% of that on the fifth cycle. These results are consistent with those obtained from cyclic voltammeter measurements (V.S.). (Note, since the test cells were not sealed during cycling, the cycle life of electrodes are not too good, but under these conditions, the test results are comparable and reliable.)

Using the double-plane model [15],  $I-t$  curves were used to calculate the  $\text{H}^+$  diffusion coefficients ( $D_{\text{H}^+}$ ). The data in Fig. 5 shows that the  $D_{\text{H}^+}$  in  $\text{MnO}_{1.78}$  and  $\text{MnO}_{1.78} + \text{Ni(OH)}_2$  electrodes do not decrease with cycle number. The first point in both curves is obtained from the electrode before the charge–discharging test. Basically, the values of  $D_{\text{H}^+}$  show either a small increase or no change with cycling.

The  $D_{\text{H}^+}$  for  $\text{MnO}_{1.78} + \text{Ni(OH)}_2$  electrode is higher than that for the  $\text{MnO}_{1.78}$  electrode. This may be due to the fact that the proton diffusion coefficient in  $\text{Ni(OH)}_2$  is much higher than that in  $\text{MnO}_2$ . Based on the data in Fig. 5, it can be concluded that the crystal structure of pr- $\text{MnO}_2$  is not cracked during cycling, irrespective of whether  $\text{Ni(OH)}_2$  is added or not. Thus, the tunnel structure for  $\text{MnO}_2$  can be maintained and the ability of proton diffusion does not decrease. On the other hand, the pr- $\text{MnO}_2$  samples have more surface OH radicals compared with  $\text{MnO}_2$ . The amount of OH radicals is related to the amount of  $\text{Mn}^{3+}$  in  $\text{MnO}_2$ .  $\text{Mn}^{3+}$  can reduce the Fermi energy of  $\text{MnO}_2$  and relax the bond of Mn–O, which decreases the hindrance for proton diffusing along C-axis. Therefore, the values of  $D_{\text{H}^+}$  do not decrease and the activity of the electrode is improved.

### 3.5. Analysis of reaction mechanism

There are different views on the nature of the reactions for the  $\text{MnO}_2$  electrochemical redox process. In general, it is

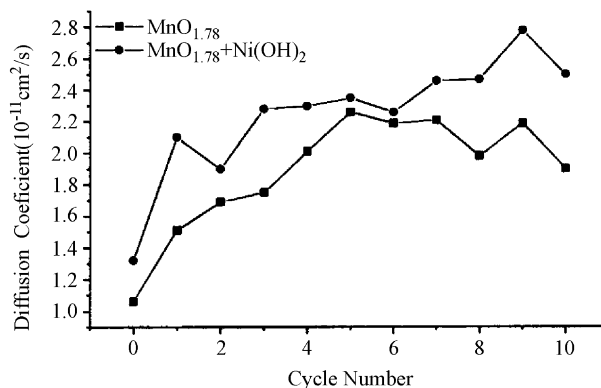
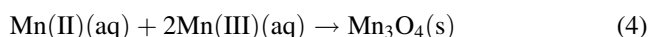


Fig. 5. Proton diffusion coefficient on each cycle of charge and discharge.

thought that the product of the first electron reduction is MnOOH, and that of the second step is Mn(OH)<sub>2</sub>, with formation of Mn<sub>3</sub>O<sub>4</sub> probably also appearing in the reaction sequence. There is no clear consensus on whether δ-, γ-, α-, or β-MnOOH is the intermediate reaction product [6,16]. We consider that partial reduction influences the crystal lattice of the intermediate product. Different crystal lattices for MnOOH have different free energies of formation and thereby, the potential of the reaction MnOOH → Mn(II) can change [6]. A less negative potential for the reaction MnOOH → Mn(II) results from partial reduction. Therefore, the formation of the manganous ion is very limited before the scanning electrode potential arrives at -0.4 V (versus Hg/HgO), so that the following reaction cannot occur [17]:



Therefore, the formation of Mn<sub>3</sub>O<sub>4</sub> can be prevented. For a similar reason, Ni(OH)<sub>2</sub> delays the 2e<sup>-</sup> discharge of MnO<sub>2</sub> [1] and decreases the opportunity for the co-existence of soluble Mn(III) ions and Mn(II) ions. Therefore, Ni(OH)<sub>2</sub> additive also prevents the formation of Mn<sub>3</sub>O<sub>4</sub>.

#### 4. Conclusions

Partially reduced samples of MnO<sub>2</sub> have been prepared by using hydrazine hydrate as a reducing reagent. Cyclic voltammograms show that the reversibility of the MnO<sub>2</sub> electrode is improved by means of using such samples. The rate and amount of formation of the electrochemically inactive Mn<sub>3</sub>O<sub>4</sub> during the scanning procedure is less than that found with MnO<sub>2</sub>. The partial reduction should not destroy the crystal lattice of MnO<sub>2</sub>, i.e. the degree of

reduction should not be less than MnO<sub>1.60</sub>. The improved performance of partially reduced MnO<sub>2</sub> is due to transformation of the crystal lattice of the intermediate reaction product. The formation of manganous ions is very limited before the scanning electrode potential arrives at -0.4 V (versus Hg/HgO) and thus the formation of Mn<sub>3</sub>O<sub>4</sub> is prevented.

The addition of Ni(OH)<sub>2</sub> to partially reduced MnO<sub>2</sub> further improves the reversibility and performance of the MnO<sub>2</sub> electrode. Ni(OH)<sub>2</sub> can delay the 2e<sup>-</sup> discharge and decrease the opportunity for the co-existence of Mn(III) ions and Mn(II) ions, and prevent the formation of Mn<sub>3</sub>O<sub>4</sub>.

#### References

- [1] X. Xia, Z. Guo, J. Electrochem. Soc. 144 (1997) L213.
- [2] Z. Guo, X. Xia, J. Appl. Sci. 18 (2000) 179 (in Chinese).
- [3] Z. Guo, X. Xia, J. Appl. Electrochem. 29 (1999) 1417.
- [4] Z. Guo, X. Xia, Dianchi (Battery Bimonthly) 27 (1997) 54 (in Chinese).
- [5] D. Qu, J. Appl. Electrochem. 29 (1999) 511.
- [6] J. McBreen, Electrochim. Acta 20 (1975) 211.
- [7] Iu.K. Kordesch (Ed.), Batteries, Vol. 1, JEC Press, Cleveland, OH, 1975, p. 488.
- [8] X. Xia, D. Shu, Dianchi (Battery Bimonthly) 23 (1993) 51 (in Chinese).
- [9] A. Kozawa, R.A. Powers, J. Electrochem. Soc. 113 (1966) 870.
- [10] G.S. Bell, K. Huber, J. Electrochem. Soc. 111 (1964) 1.
- [11] A. Kazawa, R.A. Powers, Electrochem. Technol. 114 (1967) 5535.
- [12] J.P. Gabano, B. Morigat, B.F. Laurent, Power Sources 3 (1966) 49.
- [13] W.C. Maskell, J.A.E. Shaw, F.L. Tye, Electrochim. Acta 26 (1981) 1403.
- [14] J.B. Fernerds, B.D. Resai, V.N. Karal Palal, Electrochim. Acta 29 (1984) 189.
- [15] H. Zhang, Z. Chen, X. Xia, J. Electrochem. Soc. 13 (1989) 2771.
- [16] X. Xia, Q. Li, Dianchi (Battery Bimonthly) 22 (1992) 177 (in Chinese).
- [17] M. Bode, C. Cachet, S. Bach, J.P. PeriraRamos, J.C. Glnoux, L.T. Yu, J. Electrochem. Soc. 144 (1997) 792.