

Characterization of the Bismuth-Modified Manganese Dioxide Cathodes in Rechargeable Alkaline Cells

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Bismuth-modified manganese dioxide (BMD) cathodes are shown to exhibit good cycling characteristics with a theoretical two-electron capacity in rechargeable alkaline cells. With an aim to understand the discharge-charge mechanisms, the BMD cathodes are characterized by X-ray diffraction, scanning electron microscopy, and wet-chemical analysis at various levels of discharge and charge during the first two cycles and after various numbers of cycles. It is found that a well-ordered, crystalline birnessite MnO₂ is formed at the end of first charge, irrespective of the initial form of the manganese oxide. The discharge-charge mechanism involves a reversible conversion of birnessite MnO₂ to MnOOH to Mn(OH)₂ in the subsequent cycles. Wet-chemical analyses demonstrates for the first time that the discharge/charge process in rechargeable alkaline cells involves a reversible dissolution/incorporation of K⁺ ions from/into the cathode lattice into/from the electrolyte. The incorporation of the K⁺ ions into the lattice appears to stabilize a well-ordered birnessite structure during charge. (© 2002 The Electrochemical Society. [DOI: 10.1149/1.1459713] All rights reserved.

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The rapid growth in portable electronic devices and the desire to develop electric vehicles have created enormous worldwide activity in the development of advanced, high-energy-density battery systems. Cost, environmental issues, and safety characteristics of the batteries are important considerations for large-volume consumer applications such as electric vehicles. Although the nonaqueous electrolyte-based lithium-ion cells offer higher energy density compared to other commercially available rechargeable systems, the high cost and toxicity of the currently used cobalt oxide cathodes and the safety issues are of some concern in developing these cells for electric vehicles. In this regard, aqueous systems based on inexpensive electrode materials and offering energy densities comparable to lithium-ion cells would be attractive. However, the aqueousbased systems are limited in their cell voltage and therefore the high energy density needs to be realized with electrodes having high specific capacity. For example, electrode materials involving reversible redox reactions with two electrons per transition metal ion can offer energy densities comparable to the currently available lithiumion cells. For comparison, the lithium cobalt oxide used in commercial lithium-ion cells exhibits a practical capacity corresponding to 0.5 electrons per Co.

Aqueous alkaline primary cells based on manganese dioxide cathodes are widely used for consumer applications, as manganese is inexpensive and environmentally benign. However, the use of manganese oxide cathodes for alkaline secondary batteries is still challenging because of the poor reversibility of the reduction/ oxidation process involving two electrons per Mn. Reduction beyond the one-electron level leads to the formation of oxides such as Mn_2O_3 and Mn_3O_4 that have poor rechargeability. Wroblowa *et al.*¹⁻⁶ at Ford Motor Company demonstrated more than a decade ago that the addition of bismuth by chemical modification changes the mechanism of the MnO_2 reduction/oxidation process and thereby makes it possible to reversibly discharge/charge MnO_2 cathodes over two-electron capacity. Prior to the work at Ford, Kordesch *et al.*⁷⁻¹⁰ had shown that the γ -MnO₂ is rechargeable up to a considerable number of cycles only if the discharge depth is limited to less than 35% of one-electron capacity.

With an aim to understand the mechanism of the redox process, several groups have investigated the manganese dioxide cathodes in secondary alkaline cells.¹¹⁻²⁴ There is general agreement that the two-electron reduction of manganese dioxide in alkaline medium

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takes place in two steps as proposed by Kozawa *et al.*¹⁶⁻²¹ The firstelectron reduction called the "electron-proton insertion process" involves the insertion of protons from the electrolyte into the γ -MnO₂ structure and the reduction reaction can be represented as

$$MnO_2 + H_2O + e^- \rightarrow MnOOH + OH^-$$
[1]

During this reduction process, the potential decreases continuously with composition, indicating a single-phase reaction mechanism. Therefore, the first-electron reduction is also called a homogeneous reduction process.

At the end of the first-electron reduction, the Mn^{3+} ions begin to dissolve from the cathode into the electrolyte. During the secondelectron reduction, the Mn^{3+} ions are reduced to Mn^{2+} ions by charge transfer on the surface of the conducting graphite present in the cathode mix. Since the solubility of Mn^{2+} ions in alkaline medium is relatively low compared to that of Mn^{3+} ions, the Mn^{2+} ions precipitate as $Mn(OH)_2$ phase on the surface of the graphite particles. Therefore, this second-electron reduction is called "dissolution and precipitation" process. The potential during this process remains constant with composition, and therefore this is also called a heterogeneous reduction process.

The reduction products of γ -MnO₂ cathodes in alkaline cells have been investigated by McBreen^{25,26} using X-ray diffraction (XRD) in conjunction with slow scan cyclic voltammetry and his results agree well with the mechanism proposed by Kozawa and Yeager.¹⁶ McBreen²⁵ has shown that the initial reduction involves the incorporation of protons into the γ -MnO₂ lattice, leading to the formation of an amorphous α -MnOOH phase. Further reduction of the amorphous phase yields Mn(OH)₂. On reversing the redox process, Mn(OH)₂ is oxidized initially to β -MnOOH, γ -MnOOH, and γ -Mn₂O₃ phases and further oxidation results in the formation of birnessite δ -MnO₂ phase.

However, McBreen's work^{25,26} has focused mainly on the redox process of γ -MnO₂. Following the report of Wroblowa and Gupta² on bismuth-modified manganese dioxide (BMD) materials, a considerable amount of work has been carried out by several groups²⁷⁻³⁵ in order to understand the mechanism of the redox process and the role of Bi³⁺ ions on the rechargeability. Conway *et al.*²⁷⁻²⁹ have studied BMD samples obtained by coprecipitation and electrodeposition methods. They have shown that the dissolution and precipitation is an important part of the reduction process and suggested that bismuth may help to enhance the nucleation and growth of solid species from the soluble intermediates and thereby avoid the formation of Mn₃O₄ phase. Various techniques such as cyclic voltamme-

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Sample	Chemical formula	Composition (wt %)				(Mrs/Di)
		Mn	Bi	К	H ₂ O	mole ratio
HSA	$K_4BiMn_{16}O_x \cdot 10H_2O$	46	10	7.5	9	~16
LSA	$MnO_x + Bi_2O_3$	54	11.5	0	<0.5	~16

Table I. Chemical compositions of HSA and LSA samples.

try, species detection using sensing electrodes, and UV-visible spectroscopy have been used to determine the intermediate species and to study the reaction mechanism of two-electron cycling of BMD materials. Extended X-ray absorption fine structure (EXAFS) spectroscopy and X-ray absorption near edge spectroscopy (XANES) have also been used to identify the states of Bi and Mn.²³ Donne *et al.*³⁰⁻³² have studied the redox process in various forms of BMD cathodes. They concluded that birnessite-type MnO₂ results in the formation of electrochemically inactive Mn₃O₄ at deeper discharge and the presence of Bi³⁺ ions suppresses the formation of Mn₃O₄ phase. Thus, it is generally accepted that the presence of bismuth avoids the formation of the electrochemically inactive Mn₃O₄ phase and thereby makes the MnO₂ materials rechargeable.

However, it is commonly believed in the literature that the rechargeable alkaline manganese dioxide cells require a high amount of carbon (approx. 90 wt %) as a conducting substrate in the cathode to achieve good cyclability. Cells made with such a high amount of carbon with 10% active material will have very low specific capacity and are unsuitable for commercial applications. Interestingly, RBC Technologies has been successful recently in achieving good electrochemical performance for the two-electron process with much higher loading (50-75 wt %) of active materials and thus rechargeable alkaline cells based on manganese oxides are promising.

The objective of the present investigation is to have a further understanding of the reduction/oxidation mechanism of the BMD materials at higher loading and develop optimum cathodes for rechargeable alkaline cells. Toward this task, we have investigated two different types of BMD cathodes developed at the RBC Technologies: (*i*) high surface area (HSA) Bi-birnessite type material, and (*ii*) low surface area (LSA) MnO_2 (with small amounts of Mn_2O_3 phase) + Bi₂O₃ mixture made by thermal decomposition of corresponding nitrates. This paper focuses on the phase evolution, compositional changes, and microstructural changes of the BMD cathodes during the discharge-charge process and cycling.

Experimental

The HSA samples were synthesized by a chemical route described earlier.36,37 It involves the addition of excess KOH solution to a solution of Mn(NO₃)₂ and Bi(NO₃)₃ to obtain a hydroxide gel, followed by a conversion of the gel into the oxide by passing gaseous oxygen. This sample was found to have a surface area of approximately 125 m^2/g . The chemical composition of the sample is given in Table I. The LSA samples were synthesized by a thermal decomposition of an aqueous mixture consisting of Bi(NO₃)₃ and Mn(NO₃)₂. 1 kg Mn(NO₃)₂ was dissolved in 1600 mL distilled water, and 85.4 g Bi(NO₃)₃ was dissolved in a mixture consisting of 372 mL distilled water and 128 mL nitric acid. The two solutions were then mixed together and heated first at 125°C overnight and then at 325°C for 5 h. The resulting material was then ground with a mortar and pestle and sieved using a 200 mesh screen. The dry material thus obtained had a surface area of approximately 5 m^2/g . The chemical composition is given in Table I.

Crystal structures and the degree of crystallinity of the samples were characterized by XRD. The X-ray patterns were recorded with a very slow scan rate involving a counting time of 10 s per 0.02°. The slow scan rate was necessary to have an accurate analysis of the phases present. Chemical compositions were determined by atomic



Figure 1. Discharge and charge profiles of BMD cathodes at 60% loading and C/2 rate: (a) first charge and second discharge curves of HSA sample, (b) second charge and third discharge curves of LSA sample, (c) fiftieth discharge/charge curves of HSA sample, and (d) fiftieth discharge/charge curves of LSA sample.



Figure 2. Electrochemical cycling performance (C/2 rate) of the HSA and LSA cathodes at 60% loading.

absorption spectroscopy (AAS). The solutions for AAS were prepared by digesting the discharged/charged cathode with dilute hydrochloric acid and removing the insoluble graphite and binder by filtration. Microstructural analysis and compositional mapping were carried out with a LEO 1530 scanning electron microscope (SEM) equipped with energy-dispersive spectroscopic (EDS) analysis.

Electrochemical cycling experiments were conducted with both the HSA and LSA materials at 50-65% loading, the balance being carbon and binder. Half-cells were made with BMD cathode as the working electrode, sintered Ni(OH)₂ as the counter electrode, Hg/ HgO as the reference electrode, and 31% aqueous KOH solution as the electrolyte. The Ni(OH)₂ counter electrode involves the Ni(OH)₂/NiOOH couple similar to that in the rechargeable nickelcadmium and nickel-metal hydride batteries

$$Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^-$$
 [2]

The counter electrode contained excess $Ni(OH)_2$ and thus the cell capacity is not limited by it. The cells were cycled at C/2 rate. The HSA and LSA cathodes were discharged/charged to various depths (25, 50, 75, and 100% of the capacities shown in Fig. 1) during the first two cycles, and the products were then structurally and compositionally characterized using X-ray powder diffraction and AAS, respectively. In addition to this, the cathodes were also discharged/



Figure 3. Electrochemical cycling performance (C/2 rate) of the (a) HSA cathodes at 50% loading and (b) LSA cathodes at 65% loading.



Figure 4. XRD patterns of HSA cathodes at various levels of discharge during the first cycle: (a) 0, (b) 25, (c) 50, (d) 75, and (e) 100% discharge; (\bigcirc) birnessite, (\bullet) Mn(OH)₂ or MnOOH, (*) Mn₃O₄, and (\blacklozenge) graphite.

charged to various numbers of cycles and the cycled cathodes were characterized by X-ray powder diffraction and AAS.

Results and Discussion

Electrochemical characterization.—Figure 1 shows the discharge-charge curves of half-cells made with HSA and LSA cathodes at 60% loading and cycled at C/2 rate (based on 445 mAh/g for HSA and 475 mAh/g for LSA cathodes) between the potentials of 0.35 and -1.1 V with reference to the Hg/HgO electrode. The data in Fig. 1a corresponds to the first charge and second discharge cycle of the HSA sample and that in Fig. 1b corresponds to the second charge and third discharge cycle of the LSA sample. These cycles were chosen as they show the highest discharge capacity that is evident from the cyclability data given in Fig. 2. Additionally, the first discharge profile, particularly for the LSA sample, was different from the subsequent discharge profiles as the initial phases are different from those formed after the first charge and is not included in Fig. 1 for clarity (see later). Figure 1c and d shows the charge/ discharge curves for the fiftieth cycle of the HSA and LSA samples. The data show that the discharge capacity during the fiftieth cycle (Fig. 1c and d) occurs at a slightly lower average voltage compared to that found during the initial cycles (Fig. 1a and b). The decrease in the average working voltage with cycle number is due to the increase in cell impedance. The reduction of the Mn³⁺ species occurs on the surface of the conductive carbon,^{28,34} resulting in a coating of the carbon surface by manganese species and a loss of conductive pathways with cycling. Additionally, the large volume changes accompanying the reduction of Mn^{4+} to Mn^{2+} may cause a

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Figure 5. XRD patterns of HSA cathodes at various levels of charge during the first cycle: (a) 0, (b) 25, (c) 50, (d) 75, and (e) 100% charge; (\bigcirc) birnessite, (\bigcirc) Mn(OH)₂ or MnOOH, (*) Mn₃O₄, and (\blacklozenge) graphite.

breakdown of the contact between the carbon particles with cycling. These factors lead to the development of impedance with cycling. Furthermore, the capacity utilization (number of cyclable electrons) and the average working voltage also depend on the amount of carbon present. As the active material loading increases, the internal resistance increases and the capacity utilization and working voltage decrease. In this regard, the data shown in Fig. 1 (60% active material loading) are quite different from that of Wroblowa *et al.*,¹⁻⁶ who reported a cycling of 1.9 electrons at 10% active material loading.

Figures 2 and 3 show the cyclability data of HSA and LSA cathodes. The data demonstrate that good cycling performance can be



Figure 6. Electrochemical cyclability data of Mn_3O_4 and a mixture of Mn_3O_4 and Bi_2O_3 : (\blacklozenge) Mn_3O_4 and (\bigcirc) $Mn_3O_4 + Bi_2O_3$.



Figure 7. XRD patterns of a mechanical mixture of $Mn_3O_4 + Bi_2O_3$ (a) before discharge (as-prepared) and (b) after fifth charge illustrating the formation of birnessite MnO_2 as the mixture is cycled: (\bigcirc) birnessite, (*) Mn_3O_4 , (\blacksquare) Bi_2O_3 , and (\blacklozenge) graphite.

achieved at high loading (50-65%) of active materials. The cathodes retain more than 80% of their initial capacity over 300 cycles at 50% loading (Fig. 3a) and over 200 cycles at 65% loading (Fig. 3b). These levels of loading and cycle life are attractive for developing practical cells with high energy density. The good cycling characteristics achieved with these cathodes at higher loading motivated us to further investigate the reduction and oxidation mechanism of these cathode materials. The characterizations of the cathodes with 60% loading are presented in the following sections. However, it should be noted that these BMD cathodes (HSA and LSA cathodes) could not be cycled for more than 20 or 30 cycles against zinc anodes as the dissolved zincate ions combine with the manganese ions to give inactive zinc-manganese species during the second-electron discharge process of the BMD cathode.

Structural characterization during the first two cycles.—With an objective to understand the discharge-charge mechanisms, the HSA and LSA cathodes (60% loading) were subjected to various levels (25, 50, 75, and 100% of the capacities shown in Fig. 1a and b) of discharge and charge and characterized. Figures 4 and 5 show the XRD patterns of the HSA cathodes during the first discharge-charge cycle at various levels of discharge and charge. An analysis of the X-ray data shows that the fresh (0% discharge) HSA cathode consists of a poorly crystalline birnessite MnO_2 phase (δ - MnO_2) in addition to a few reflections corresponding to graphite. While no noticeable change occurs in the XRD pattern at 25% discharge (Fig. 4b), the reflections corresponding to the birnessite MnO_2 phase van-



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Figure 8. XRD patterns of HSA cathodes at various levels of discharge during the second cycle: (a) 0, (b) 25, (c) 50, (d) 75, and (e) 100% discharge; (\bigcirc) birnessite, (\bullet) Mn(OH)₂ or MnOOH, (*) Mn₃O₄, (\blacksquare) Bi, and (\blacklozenge) graphite.

ishes and new reflections corresponding to Mn_3O_4 phase occur at 50% discharge (Fig. 4c). At 50% discharge, reflections corresponding to MnOOH are not apparent possibly due to the poor crystallinity or amorphous nature. On further discharge to 75% (Fig. 4d), reflections corresponding to $Mn(OH)_2$ begin to appear and the fully (100%) discharged cathode (Fig. 4e) consists of both $Mn(OH)_2$ and Mn_3O_4 . However, the amount of Mn_3O_4 in the 100% discharged sample (Fig. 4e) appears to be lower than that found in the 50% discharged sample (Fig. 4c), as indicated by a slight decrease in the intensity of the reflections corresponding to Mn_3O_4 . Thus, on going from 50 to 100% discharge, a small fraction of the Mn_3O_4 may possibly undergo reduction.

On charging the discharged cathodes (Fig. 5), $Mn(OH)_2$ vanishes and birnessite MnO_2 phase is formed. At 25% charge (Fig. 5b), the pattern shows reflections corresponding to only $Mn(OH)_2$ and Mn_3O_4 phases in addition to graphite. At 50% charge (Fig. 5c), the birnessite MnO_2 phase begins to appear and then continues to grow while the amount of $Mn(OH)_2$ or MnOOH decreases with further charge (Fig. 5d). It is possible that a small amount of crystalline β -MnOOH, whose strongest reflection overlaps with the strongest reflection of $Mn(OH)_2$ at around $2\theta = 20^\circ$, may be present in the 25-75% charged samples. This may be particularly true in the 75% charged sample as indicated by the presence of a weak reflection at around $2\theta = 20^\circ$ (Fig. 5d), since no $Mn(OH)_2$ is expected to be present at this depth of charge. The fully charged cathode (100%) consists of mostly a well-ordered crystalline birnessite MnO_2 phase

Figure 9. XRD patterns of HSA cathodes at various levels of charge during the second cycle: (a) 0, (b) 25, (c) 50, (d) 75, and (e) 100% charge; (\bigcirc) birnessite, (\bullet) Mn(OH)₂ or MnOOH, (*) Mn₃O₄, (\blacksquare) Bi, and (\blacklozenge) graphite.

apart from graphite. Thus, at the end of the first discharge-charge cycle (Fig. 5e), a well crystalline and ordered birnessite MnO_2 phase is formed, even though the initial cathode consisted of a poorly crystalline birnessite MnO_2 phase (Fig. 4a). More importantly, the Mn_3O_4 that is present at the end of first discharge (Fig. 4e or 5a) vanishes completely at the end of first charge (Fig. 5e). This observation reveals that the presence of bismuth that is in intimate contact with the Mn_3O_4 helps to recharge the Mn_3O_4 to birnessite MnO_2 .

To understand this point further, we have carried out discharge/ charge cycling experiments with cells fabricated with conventional Mn_3O_4 and a physical mixture consisting of conventional Mn_3O_4 and 10 wt % Bi_2O_3 ; the cycling data are given in Fig. 6. While Mn_3O_4 shows little reversible capacity in the absence of bismuth, it shows a gradual increase in capacity in the presence of bismuth. As the $Mn_3O_4 + Bi_2O_3$ mixture is cycled, more and more manganese oxide becomes in intimate contact with bismuth and thereby participates in the reversible discharge/charge process. Additionally, the XRD data shown in Fig. 7 illustrate that Mn_3O_4 is transforming to birnessite MnO_2 during cycling in the presence of bismuth. The data in Fig. 6 and 7 clearly demonstrate that while pure Mn_3O_4 is difficult to recharge, the presence of bismuth in intimate contact results in good rechargeability.

Figures 8 and 9 show the XRD patterns of the HSA cathodes during the second cycle at various levels of discharge and charge. During the second discharge, the birnessite MnO_2 vanishes and $Mn(OH)_2$ is formed. At 25% discharge (Fig. 8a), a reflection begins to occur at around $2\theta = 20^\circ$, which could be due to the formation





Figure 10. XRD patterns of LSA cathodes at various levels of discharge during the first cycle: (a) 0, (b) 25, (c) 50, (d) 75, and (e) 100% discharge; $(\Box) \gamma$ -MnO₂, (\bullet) Mn(OH)₂ or MnOOH, (θ) Mn₂O₃, (\blacksquare) Bi or Bi₂O₃, (*) Mn₃O₄, and (\blacklozenge) graphite.

of β -MnOOH, since Mn(OH)₂ is not expected to be formed at this discharge level. However, a similar reflection was not observed at 25% discharge during the first discharge cycle (Fig. 4b), possibly due to a poor crystallinity of the β -MnOOH or the absence of the formation of crystalline β -MnOOH during the first discharge cycle. It is possible that the formation of a well-ordered crystalline birnessite MnO₂ phase at the end of first charge (Fig. 5e) may help to form the crystalline β -MnOOH phase or improve the crystallinity of the β-MnOOH phase formed during the second discharge. It suggests that the crystallinity of the reduction/oxidation products depends on the crystallinity of the material in the preceding stage. At 50% discharge (Fig. 8c), reflections corresponding to Mn₃O₄ appear and the cathode consists of birnessite MnO_2 Mn_3O_4 , and β -MnOOH [or $Mn(OH)_2$] phases. On further discharge, the amount of birnessite MnO₂ decreases and the fully discharged cathode (Fig. 8e) consists of Mn(OH)₂ and Mn₃O₄ phases and a small amount of bismuth metal apart from graphite. More importantly, the Mn₃O₄ phase that began to appear at 50% discharge (Fig. 8c) decreases slightly at 100% discharge (Fig. 8e). Thus, part of the Mn₃O₄ undergoes reduction on going from 50-75% discharge to 100% discharge in Fig. 8, similar to that found during the first discharge in Fig. 4.

On charging back (Fig. 9), $Mn(OH)_2$ is oxidized to a wellordered birnessite MnO_2 phase and the reflections corresponding to the bismuth metal vanish due to the oxidation of metallic Bi to Bi³⁺. This indicates that bismuth also undergoes redox reactions during the discharge-charge process. At 100% charge (Fig. 9e), mostly a well-ordered crystalline birnessite MnO_2 phase apart from graphite

Figure 11. XRD patterns of LSA cathodes at various levels of charge during the first cycle: (\bigcirc) birnessite, ($\textcircled{\bullet}$) Mn(OH)₂ or MnOOH, (θ) Mn₂O₃, (\blacksquare) Bi or Bi₂O₃, (*) Mn₃O₄, and (\blacklozenge) graphite.

is present as found at the end of first charge (Fig. 5e). The Mn_3O_4 that is present at the end of second discharge (Fig. 8e or 9a) vanishes completely at the end of second charge (Fig. 9e), similar to that found during the first charge (Fig. 5e). The data confirm further that the presence of bismuth helps to recharge the Mn_3O_4 to birnessite MnO_2 .

Figures 10 and 11 show the XRD patterns of the LSA cathodes at various levels of discharge and charge, respectively, during the first cycle. The X-ray data show that the fresh (0% discharge) LSA cathode (Fig. 10a) consists of mainly γ -MnO₂ and α -Mn₂O₃ phases apart from graphite. Although the material consists of a nominal 10 wt % Bi₂O₃, X-ray data do not indicate its presence, possibly due to the poor crystallinity. The γ -MnO₂ phase has an intergrowth structure consisting of ramsdellite and pyrolusite units. The appearance of a reflection at around $2\theta = 20^{\circ}$ in the 25 and 50% discharged cathodes (Fig. 10b and c) could be due to the formation of β -MnOOH rather than Mn(OH)₂, since Mn(OH)₂ is not expected at this level of discharge. The formation of crystalline β -MnOOH during the first discharge cycle, unlike in the case of HSA cathodes, could be due to the better crystallinity of and a different form of manganese oxide $(\gamma - MnO_2)$ in the initial LSA sample that was obtained by a thermal decomposition procedure; in the case of HSA cathodes, the formation of crystalline β -MnOOH becomes apparent only during the first charge (Fig. 5) or later discharge (Fig. 8). Above 50% discharge (Fig. 10d and e), the LSA cathodes also yield Mn₃O₄ along with the Mn(OH)₂ phase. Additionally, the strongest reflections of metallic bismuth and possibly Bi2O3, which overlap at





Figure 12. XRD patterns of discharged and charged HSA cathodes before and after subjecting them to various numbers of cycles: (\bigcirc) birnessite, (\bigcirc) Mn(OH)₂ or MnOOH, (*) Mn₃O₄, (\blacklozenge) graphite, (DCh) discharge, and (Ch) charge.

around $2\theta = 28^{\circ}$, are seen clearly in the 25-100% discharged cathodes, unlike in the case of the HSA cathode where metallic bismuth reflections are seen only at the end of the second discharge (Fig. 8e). This difference could be due to the better crystallinity of and a different form of manganese oxide (γ -MnO₂ and α -Mn₂O₃) in the initial LSA sample. It is possible that the bismuth could be distributed differently in the initial LSA and HSA samples. The amount of γ -MnO₂ phase that is present in the initial LSA sample decreases during first discharge and it vanishes completely at 75-100% discharge. On the other hand, the amount of α -Mn₂O₃ appears to decrease only slightly at the end of the first discharge cycle.

On charging back the discharged cathodes (Fig. 11), the $Mn(OH)_2$ phase vanishes while the birnessite MnO_2 phase is formed, as in the case of HSA cathodes (Fig. 5). Additionally, the Mn_3O_4 that is present at the end of the first discharge (Fig. 10e or 11a) vanishes completely at the end of the first charge (Fig. 11e), indicating the rechargeability of Mn_3O_4 in the presence of bismuth, as we found with the HSA sample. At the end of first charge, a well-ordered crystalline birnessite phase is formed as in the case of HSA cathodes, even though the initial LSA sample consists of a different form of MnO_2 (γ -MnO_2) and Mn_2O_3 . During the second discharge, the birnessite MnO_2 phase is reduced to $Mn(OH)_2$ and during the second charge, the $Mn(OH)_2$ phase is oxidized back to the birnessite phase as in the case of the HSA cathode. These experiments demonstrate that a well-ordered and crystalline birnessite MnO_2 is formed at the end of first charge, which then undergoes a

Figure 13. XRD patterns of discharged and charged LSA cathodes before and after subjecting them to various numbers of cycles: (\Box) γ -MnO₂, (\bigcirc) birnessite, (\bullet) Mn(OH)₂ or MnOOH, (θ) Mn₂O₃, (\blacksquare) Bi or Bi₂O₃, (*) Mn₃O₄, (\bullet) graphite, (DCh) discharge, and (Ch) charge.

reversible redox process during the subsequent cycles as in the case of HSA samples, even though the initial LSA sample is structurally different from the initial HSA sample.

The data of HSA and LSA cathodes clearly reveal that the presence of bismuth in the BMD cathodes renders good rechargeability. As discussed earlier, this assertion is supported by the electrochemical data of a mixture consisting of conventional Mn_3O_4 and Bi_2O_3 . This mixture was found to have good rechargeability (Fig. 6) and a well-ordered, crystalline birnessite MnO_2 was formed at the end of first charge. An explanation for the formation of well crystalline birnessite MnO_2 at the end of first charge irrespective of the initial form of manganese oxide is provided in a later section.

Structural characterization of cycled cathodes.—Both the HSA and LSA cathodes were analyzed by XRD at the discharged and charged states after subjecting them to various numbers of cycles. The XRD patterns of the HSA and LSA cathodes before and after cycling are shown in Fig. 12 and 13. As discussed in the previous section, a well-ordered, crystalline birnessite MnO₂ phase is formed at the end of first charge both in the case of HSA and LSA, which then undergoes a reversible discharge-charge process during subsequent cycling. An examination of the X-ray patterns in Fig. 12 and 13 reveals that the crystallinity and amount of the birnessite MnO₂ and Mn(OH)₂ phases decreases with increasing number of cycles due to an increase in the amount of Mn₃O₄ (see the following) and a possible increase in the amorphous components. Also, the amount of Mn₂O₃ phase in the LSA cathodes (Fig. 13) decreases with in-



Figure 14. SEM photographs of the HSA cathode (a) after second charge and (b) after 40th charge. The region of bismuth clustering in the cycled electrode is indicated by a rectangle.

creasing number of cycles, indicating a participation of Mn₂O₃ in the redox process in the presence of bismuth. Although little or no Mn₃O₄ is found at the end of charge during the initial number of cycles, some amount of Mn₃O₄ is observed at the end of charge after extended cycling. However, for a given cycle, the amount of Mn₃O₄ found at the end of discharge is larger than that found at the end of charge, even after extended cycling. This observation again confirms the participation of Mn₃O₄ in the redox process even after extended cycling. The increase in the amount of Mn₃O₄ at the end of charge with cycling is due to the clustering of the bismuth metal and an isolation of the manganese oxide away from bismuth, as indicated by EDS analysis of the cycled cathodes in SEM. With a decreasing intimate contact with bismuth, the Mn₃O₄ particles become increasingly inactive during extended cycling. The increase in the amount of isolated Mn₃O₄ phase with cycling could be one of the reasons for the capacity fade found during cycling.

Microstructural and compositional characterizations.—The microstructures of both the HSA and LSA cathodes were examined by SEM equipped with EDS analysis during the first two discharge-charge cycles and at the discharged and charged states after subjecting them to various numbers of cycles. SEM data indicate the presence of hexagonal shape $Mn(OH)_2$ particles in the discharged cathodes. In addition, EDS analysis indicates a clustering of bismuth after extended cycling, as shown in Fig. 14. While the cathode after



Figure 15. Variation of potassium content in HSA cathodes with level of discharge/charge: (a) during first cycle and (b) during second cycle.

the second charge exhibits a uniform distribution of bismuth (Fig. 14a), that after the 40th charge shows a clustering of bismuth as indicated in Fig. 14b. More important, the EDS compositional mapping for Mn, O, K, Bi, and C showed some important differences between the discharged and charged cathodes. While no significant change was observed in the distribution of other elements, the amount of potassium was found to be higher in the charged state compared to that in the discharged state.

In order to have a further understanding, the potassium contents in the cathodes at various levels of discharge and charge were analyzed by AAS. The variations of potassium content with the depth of discharge and charge are shown in Fig. 15 and 16 for the HSA and LSA cathodes, respectively, during the first and second cycles. The



Figure 16. Variation of potassium content in LSA cathodes with level of discharge/charge: (a) during first cycle and (b) during second cycle.

initial HSA sample has about 7.5 wt % K and the K content decreases continuously up to 50% discharge (Fig. 15a). The sample with 50-100% discharge has around 1 wt % K. Upon charging back the discharged cathodes, the K content remains around 1 wt % up to 50% charge and thereafter increases. The fully charged cathode has around 10 wt % K, which is slightly higher than that in the initial HSA cathode. During the second cycle (Fig. 15b), the change in K content is fully reversible. In the case of LSA cathodes (Fig. 16), the K content remains around 0 wt % throughout the first discharge, since the initial LSA cathodes did not contain any K. During the first charge, the K content increases and the fully charged sample has around 8 wt % K (Fig. 16a). During the second cycle (Fig. 16b), the change in K content is nearly reversible as in the case of the HSA cathode (Fig. 15b).

The chemical analysis data clearly establish, for the first time, a change in the K content during the discharge-charge process. The data reveal dissolution of potassium from the crystal lattice into the electrolyte during discharge and an incorporation of potassium from the electrolyte into the crystal lattice during charge. We believe that the incorporation of the K⁺ ions from the electrolyte into the manganese oxide cathode is to stabilize the layered birnessite structure. It appears that the stabilization of the layered birnessite structure requires significant amount of positively charged cations, such as the K^+ ions between the layers. The presence of potassium between the layers leads to a well-ordered, crystalline birnessite phase, as evident in the XRD patterns discussed in an earlier section. In the case of an LSA cathode that does not contain potassium initially, the incorporation of potassium from the electrolyte into the LSA cathode during the first charge leads to the formation of birnessite, as illustrated by the X-ray data in Fig. 11. The chemical analysis experiments thus establish that the discharge/charge mechanism of the manganese oxide cathodes in rechargeable alkaline cells involves a dissolution/incorporation of K⁺ ions into/from the electrolyte from/ into the cathode lattice.

Conclusions

Bismuth-modified manganese dioxide cathodes have been shown to exhibit good cyclability at high (50-65%) loadings. The cathodes retain more than 80% of initial capacity over 300 cycles at 50% loading. Layered birnessite-type MnO₂ is formed after the first discharge-charge cycle irrespective of the initial form of the BMD materials. The cathodes have higher potassium content in the charged state compared to the discharged state due to an incorporation of the K⁺ ions from the electrolyte into the cathode lattice during charge. The higher potassium content in the charged state is to stabilize the layered birnessite structure. The rechargeable alkaline cells thus involve an incorporation/dissolution of potassium ions into/from the cathodes during the charge/discharge process. The presence of bismuth renders good cyclability to the manganese dioxide cathodes as well as other manganese oxides that cannot otherwise be cycled. The mechanism of BMD cycling is similar to that of EMD in the sense that it involves dissolution of Mn³⁺ intermediate and the second electron reduction is a dissolution/precipitation process. However, most of the first electron reduction in BMD occurs in a heterogeneous manner, unlike in EMD. The species that are involved during the cycling of BMD have also been identified in the literature.^{22,23,27,28,33,34} Nevertheless, the exact mechanism of bismuth participation in rendering good rechargeability to the manganese oxides remains to be established concretely.

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