

Effect of BaBiO_3 and $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ additives on the rechargeability of manganese oxide cathodes in alkaline cells

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Abstract

The effect of the incorporation of small amounts (1–5 wt%) of semiconducting BaBiO_3 and metallic $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ additives on the rechargeability of electrolytic manganese dioxide (EMD) cathodes in alkaline cells in the one-electron regime has been investigated. Both the BaBiO_3 and $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ additives lead to better cyclability compared to the previously known binary oxide additive Bi_2O_3 . X-ray diffraction patterns recorded before and after 30 cycles as well as cyclic voltammograms recorded after first and 30 cycles reveal that the better cyclability in the presence of BaBiO_3 and $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ additives is due to the suppression of the formation of unwanted, electrochemically inactive birnessite and hausmannite phases and a shifting of the second-electron capacity of Mn to higher potentials.

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1. Introduction

Rechargeable batteries based on electrolytic manganese dioxide (EMD) cathodes are attractive as Mn is inexpensive and environmentally benign with the involvement of in principle two electrons per Mn. However, the poor rechargeability of EMD has hampered the commercialization of rechargeable alkaline cells. A significant progress was made by Kordesch et al. [1–3] by devising a practical rechargeable manganese dioxide (RAM™) cell involving one electron per Mn. The one-electron process is a homogeneous reaction with a linear voltage profile involving the insertion/extraction of protons into/from the $\gamma\text{-MnO}_2$ lattice [4–7]. Although the process is reversible to some extent at lower depth of discharge (<0.5 e/Mn), a slow but steady capacity fade occurs at deep discharge (>0.5 e/Mn), which limits the service life of the cells [1–8]. Interestingly, the incorporation of small amounts of Bi- or Ba-containing compounds to EMD was found to improve the rechargeability considerably to some extent [9–11]. Our group

[12–14] recently showed from X-ray diffraction analysis of the cycled manganese oxide cathodes in the one-electron regime that the formation of electrochemically inactive phases, such as birnessite ($\delta\text{-MnO}_2$) and hausmannite (Mn_3O_4) is partly responsible for the capacity fade. Birnessite and hausmannite are formed by a disproportionation of the dissolved Mn^{3+} intermediates, and based on some designed chemical reaction experiments, we also showed that the incorporation of Bi- and/or Ba-containing compounds suppress the formation of birnessite and hausmannite by keeping the Mn^{3+} ions in solution for longer time and blocking the disproportionation reaction of Mn^{3+} .

With an aim to improve the rechargeability, the incorporation of various additives into EMD by physical and chemical mixing is being explored by various groups [15–17]. Recognizing from the previous work that the incorporation of Bi- or Ba-containing compounds improve the rechargeability [9–14], we present here the incorporation of the semiconducting barium bismuth oxide (BaBiO_3) and metallic barium potassium bismuth oxide ($\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$) in which both Ba and Bi are present in the same phase. The electrochemical evaluation as well as the origin of improvement in rechargeability is presented.

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2. Experimental

Electrolytic manganese dioxide (EMD) was supplied by Chemmetals, Inc. BaBiO_3 was prepared by heating required amounts of BaCO_3 and Bi_2O_3 at 600°C in air for 30 h with one intermittent grinding. $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ was prepared by heating required amounts of BaCO_3 , KO_2 , and Bi_2O_3 in flowing nitrogen at 725°C for 1 h followed by annealing in flowing oxygen at 550°C for 50 min [18].

Thin film type electrodes of about 5–8 mg weight were prepared by mixing the modified EMD (75 wt%) consisting of small amounts of the additives BaBiO_3 or $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ (1–5 wt%) with graphite (Timrex SFG-15, 20 wt%) and polytetrafluoroethylene (PTFE) binder (5 wt%) in a mortar and pestle, followed by rolling into thin sheets. The thin film electrode was then mounted onto a nickel mesh current collector. The electrochemical measurements were carried out with a three electrode assembly with a Hg/HgO (in 9 M KOH) reference electrode, a porous nickel counter electrode consisting of $\text{NiOOH}/\text{Ni}(\text{OH})_2$, and 9 M KOH electrolyte. The cycling experiments were carried out under constant current discharge–charge conditions in the range of -0.4 and $+0.35$ V vs Hg/HgO with discharge and charge rates of, respectively, $\text{C}/2$ and $\text{C}/4$. The cyclic voltammograms were recorded in the potential envelope of $+0.4$ and -1.0 V vs Hg/HgO at a scan rate of $40\text{ }\mu\text{V/s}$. The structural characterization of the cathode materials before and after the electrochemical tests was carried out with X-ray diffraction. The cycled cathodes were washed with deionized water and dried under vacuum at room temperature overnight before examining by X-ray diffraction.

3. Results and discussion

3.1. Cyclability

Figs. 1 and 2 compare the cyclability of EMD with various amounts (1–5 wt%) of BaBiO_3 and $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ additives with those of plain EMD and EMD containing

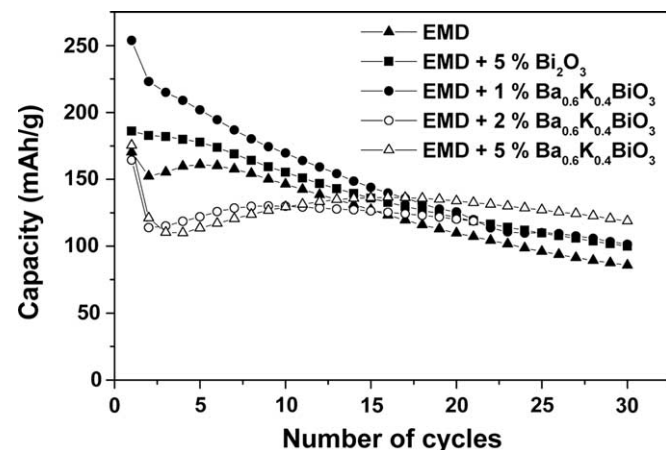


Fig. 1. Comparison of the cyclability of EMD in the presence of various amounts (1–5 wt%) of BaBiO_3 with those of plain EMD and EMD with 5 wt% Bi_2O_3 .

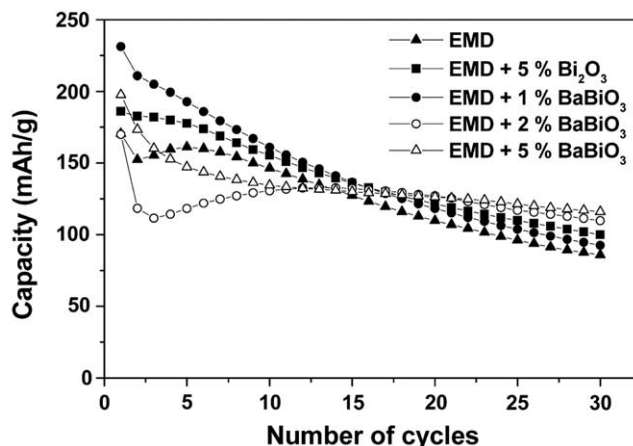


Fig. 2. Comparison of the cyclability of EMD in the presence of various amounts (1–5 wt%) of $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ with those of plain EMD and EMD with 5 wt% Bi_2O_3 .

5 wt% Bi_2O_3 . The addition of 1 wt% BaBiO_3 or $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ increases the initial capacity significantly compared to plain EMD, but does not help to improve the cyclability. In contrast, the addition of 2 or 5 wt% BaBiO_3 or $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ improves the capacity retention significantly particularly at higher number of cycles although there is a large drop in capacity during the first cycle. Thus, both the BaBiO_3 and $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ additives offer an important benefit of good long-term cyclability compared to the previously known Bi_2O_3 additive.

3.2. Structural characterization

In order to understand the origin of the better capacity retention in the presence of BaBiO_3 and $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ additives, we have focused on a comparison of the structural characterization of the cathodes before and after cycling. Fig. 3 compares the X-ray diffraction patterns of the cathodes with and without various additives before and after 30 cycles in the one-electron region (cut-off discharge voltage: -0.4 V vs Hg/HgO). While strong reflections corresponding to birnessite ($\delta\text{-MnO}_2$) and hausmannite (Mn_3O_4) phases are found in the cycled cathodes consisting of plain EMD (Fig. 3(b)) and EMD + 5 wt% Bi_2O_3 (Fig. 3(d)), only a weak reflection corresponding to birnessite is found in the case of the cathode consisting of EMD + 5 wt% BaBiO_3 (Fig. 3(g)). More importantly, no reflections corresponding to both birnessite and hausmannite are found in the case of the cathode consisting of EMD + 5 wt% $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ (Fig. 3(j)). The results suggest that both the BaBiO_3 and $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ additives suppress the formation of the unwanted, electrochemically inactive birnessite and hausmannite phases, but the latter is much more effective than the former. Thus, the better cyclability in the presence of the BaBiO_3 and $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ additives at higher number of cycles is related to the suppression of the formation of the electrochemically inactive birnessite and hausmannite phases [12–14].

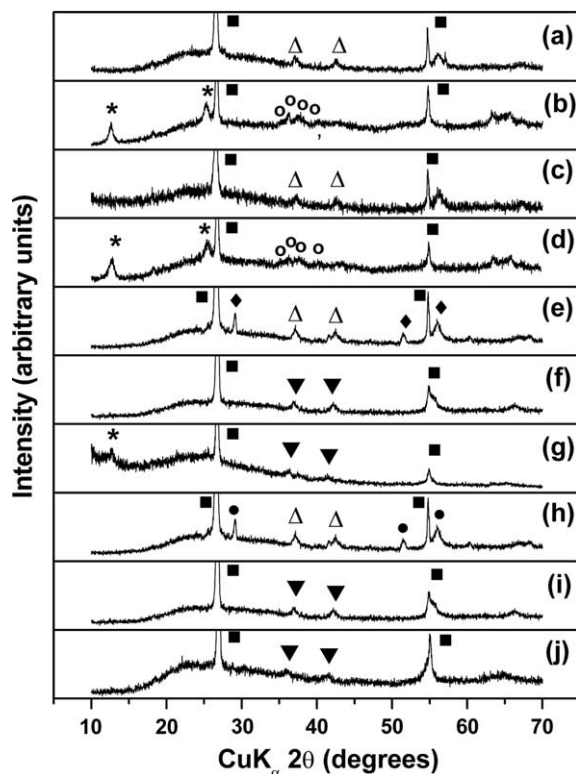


Fig. 3. X-ray diffraction patterns recorded in the charged state before and after various number of cycles (0–30 cycles): (a) plain EMD before cycling, (b) plain EMD after 30 cycles, (c) EMD with 5 wt% Bi_2O_3 before cycling, (d) EMD with 5 wt% Bi_2O_3 after 30 cycles, (e) EMD with 5 wt% BaBiO_3 before cycling, (f) EMD with 5 wt% BaBiO_3 after two cycles, (g) EMD with 5 wt% BaBiO_3 after 30 cycles, (h) EMD with 5 wt% $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ before cycling, (i) EMD with 5 wt% $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ after two cycles, (j) EMD with 5 wt% $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ after 30 cycles. ■, Δ, ▼, ◆, ●, * and ○ refer to graphite, $\delta\text{-MnO}_2$, $\gamma\text{-MnOOH}$, BaBiO_3 , $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$, birnessite, and hausmannite, respectively.

3.3. Cyclic voltammetry

With an aim to develop a further understanding, we have also focused on a comparison of the cyclic voltammograms (CV) of the cathodes with and without the various additives after galvanostatically cycling (1–30 cycles) them in the one-electron regime (cathodic cut-off potential: -0.4 V) and the CV plots are given in Fig. 4. The ratio of charge associated with the cathodic peak C_1 (corresponds to the reduction of Mn^{4+} to Mn^{3+}) to the anodic peaks A_1 and A_2 (correspond to the two-step oxidation of Mn^{2+} to Mn^{4+}) is defined hereafter as the percentage (%) two-electron capacity. The CV profiles obtained for the plain EMD and the EMD + Bi_2O_3 cathodes are consistent with the literature reports [19–22]. After the first cycle, plain EMD has a % two-electron capacity value of 50 (Fig. 4(a)) since the second-electron reduction (Mn^{3+} to Mn^{2+} and peak C_2) takes place at a far negative potential, viz. -0.5 to -0.8 V and its contribution at a cathodic cut-off potential of $\geq -0.4\text{ V}$ is not available. On the other hand, the cathode with 5 wt% Bi_2O_3 has a % two-electron capacity value of 74 above a potential of $\geq -0.6\text{ V}$ with a

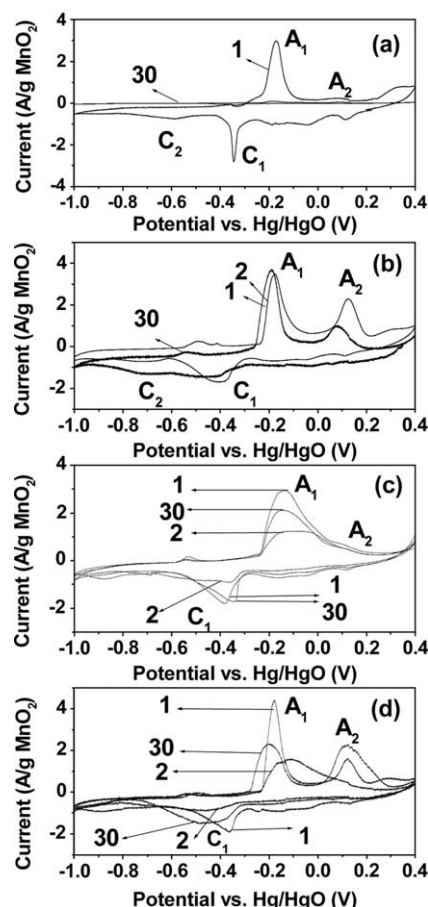


Fig. 4. Cyclic voltammograms (CV) recorded in 9 M KOH at a sweep rate of $4 \times 10^{-5}\text{ V/s}$ after cycling the electrodes galvanostatically in the one-electron region (cut-off discharge voltage: -0.4 V vs Hg/HgO): (a) plain EMD, (b) EMD + 5 wt% Bi_2O_3 , (c) EMD + 5 wt% BaBiO_3 , and (d) EMD + 5 wt% $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$. The numbers refer to the number of galvanostatic discharge-charge cycles before recording the CV.

broad peak for C_1 (Fig. 4(b)) after the first cycle, indicating the availability of part of the second-electron capacity at potentials of $\geq -0.6\text{ V}$ (peak C_1). After extensive cycling (30 cycles), the CV profile of plain EMD shows a decrease in the current response (Fig. 4(a)) due to an accumulation of the electrochemically inactive phases, birnessite and hausmannite (Fig. 3(b)), resulting in a capacity fade. On the other hand, in the presence of Bi_2O_3 additive, the cathodic peak C_1 after two cycles remains similar to that observed after the first cycle, but becomes resolved into two peaks after 30 cycles (Fig. 4(b)), which is consistent with the previous literature [2]. The slow splitting or resolution of the peak C_1 as the sample is cycled and the formation of the inactive birnessite and hausmannite phases result in a slow decrease of the contribution of the second-electron capacity at $\geq -0.4\text{ V}$. Thus, the benefit provided by the Bi_2O_3 additive decreases with cycling, resulting in a continuous capacity fade on cycling the cathodes at $\geq -0.4\text{ V}$ as seen in Figs. 1 and 2.

The cathodes with 5 wt% BaBiO_3 and $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ have % two-electron capacity values of, respectively, 62

and 74 (Figs. 4(c) and (d)) after the first discharge–charge cycle, indicating the availability of part of the second-electron capacity at potentials of ≥ -0.4 V similar to that found with the EMD + Bi_2O_3 cathode. However, the CV profiles change after subjecting the cathodes for discharge–charge cycling. For example, the CV profiles after the second cycle show lower current response with slightly resolved, broad cathodic peaks compared to that after the first cycle. This results in a decrease in the contribution of the second electron to the capacity at potentials of ≥ -0.4 V (peak C_1) after the first cycle and a consequent large decrease in capacity value on going from first to second cycle in Figs. 1 and 2. However, after extensive cycling (30 cycles), the current response increases compared to that after two cycles in the case of $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ -modified EMD (Fig. 4(d)) while the original CV profile is almost restored with an increase in the current response compared to that after two cycles in the case of BaBiO_3 -modified EMD (Fig. 4(c)), indicating the regaining of the second-electron contribution to the capacity. This is well reflected in the cyclability curves of the cathodes consisting of 2–5 wt% BaBiO_3 and $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ (Figs. 1 and 2), where a decrease in the capacity values observed during the initial cycles is followed by an increase in the capacity values at higher number of cycles.

Additionally, the reflections corresponding to the BaBiO_3 and $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ additives are suppressed on going from first cycle (Figs. 3(e) and (h)) to second cycle (Figs. 3(f) and (i)) and vanish completely on going to 30 cycles (Figs. 3(g) and (j)). This could be due to the reaction of the additives with the electrolyte or amorphization of the additives during the first few cycles. The decrease in the current response of peak C_1 in the CV on going from first cycle to second cycle could also be related to this. However, as the electrode is cycled, possibly the newly formed Bi- and/or Ba-containing species seem to help to suppress the formation of the inactive birnessite and haumannite phases and render good capacity retention.

4. Conclusions

The incorporation of small amounts (2–5 wt%) of semi-conducting BaBiO_3 and metallic $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ additives into EMD improves the rechargeability significantly in the one-electron regime after a large drop in capacity between the first and second cycle compared to that found with the previously known additive Bi_2O_3 . The enhanced

rechargeability is found to be due to the suppression of the formation of unwanted, electrochemically inactive birnessite and haumannite phases and the shifting of the second-electron capacity to higher potentials. The study demonstrates that identification of potential additives through a systematic investigation could enhance the commercial feasibility of rechargeable alkaline cells based on the inexpensive and environmentally benign manganese oxide cathodes.

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