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Effect of Multiple Cation Electrolyte Mixtures on Rechargeable Zn–MnO₂ Alkaline Battery

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A Bi₂O₃ in β -MnO₂ composite cathode material has been synthesized using a simple hydrothermal method and cycled in a mixed KOH–LiOH electrolyte with a range of concentrations. We show that, at a KOH:LiOH molar ratio of 1:3, both proton insertion and lithium insertion occur, allowing access to a higher fraction of the theoretical capacity of the MnO₂ while preventing the formation of ZnMn₂O₄. This enables a capacity of 360 mAh/g for over 60 cycles, with cycling limited more by anode properties than traditional cathodic failure mechanisms. The structural changes occurring during cycling are characterized using electron microscopy and in situ synchrotron energy-dispersive X-ray diffraction (EDXRD) techniques. This mixed electrolyte shows exceptional cyclability and capacity and can be used as a drop-in replacement for current alkaline batteries, potentially drastically improving their cycle life and creating a wide range of new applications for this energy storage technology.

Manganese–zinc primary alkaline batteries are a ubiquitous power source for a wide range of electronic devices today. These types of cells have high theoretical capacity and energy density, coupled with low cost, and are potentially suitable for a wide range of applications, including renewable energy storage and other grid applications, due to their high capacity, fast ionic conductivity, and low cost.(1) However, these types of cells have a wide range of different failure mechanisms, which taken as a whole prevent their effective use as secondary batteries.

Many of these failure mechanisms are associated with phase transformations in the electrolytic γ -MnO₂ cathode. In Figure 1, we summarize the irreversible reaction of electrochemically prepared γ -MnO₂ (EMD) in an alkaline battery, as previously reported in the literature.(2-6)

Figure 1. Reaction mechanism of γ -MnO₂ cathode in a standard alkaline battery.

The most commonly accepted model of the phase transformation process proposes that the initial γ -MnO₂ structure, which contains a 2×1 and 1×1 tunnel structures, is transformed into α -MnOOH and γ -MnOOH during the first electron reduction.(2-4) Proton intercalation can lead to the formation of either α -MnOOH, which maintains the 2×1 tunnel structure of γ -MnO₂, or to the 1×1 tunnel structured γ -MnOOH, during which transformation the rearrangement of Mn–O bonding occurs simultaneously with proton intercalation. In these phases, protons are complexed with the Mn atom, reducing the Mn oxidation state from 4+ to 3+. During the second electron reduction, Mn₃O₄(4, 5) and Mn(OH)₂(5, 6) are produced. If zinc is present in the electrolyte, ZnMn₂O₄ is produced instead.(7) ZnMn₂O₄ is not presented in Figure 1, as its formation from MnOOH, via the pathway $2\text{MnOOH} + \text{Zn(OH)}_4^{2-} \rightarrow \text{ZnMn}_2\text{O}_4 + 2\text{H}_2\text{O} + 2\text{OH}^-$, is not an electrochemical process, and it is not considered to be an electrochemically active compound.(8, 9, 11)

Upon charging of the fully reduced phase, Mn(OH)₂ is converted to β -MnOOH, γ -MnOOH, and γ -Mn₂O₃, and subsequently to δ -MnO₂, also called birnessite.(6) δ -MnO₂ is a layered structure which may incorporate various cations, structural water, or both in the interlayer spacing, depending on the synthesis conditions.(10)

The irreversibility of MnO₂ is strongly correlated with the formation of the spinel phases Mn₃O₄ and ZnMn₂O₄, as shown in Figure 1. Once Mn₃O₄ is generated during the first discharge, this phase can only be partially reduced to Mn(OH)₂, and much of the produced spinel remains in the electrode even when it is fully discharged.(5) Meanwhile, ZnMn₂O₄ cannot be reduced to Mn(OH)₂ at all. During the first charge, only the oxidized Mn(OH)₂ is converted to MnOOH and δ -MnO₂, while the spinel phases have been found to be electrochemically inactive during oxidation.(6, 12) After the first cycle, the cell will progressively lose capacity as more and more Mn₃O₄ is generated, leading to uneven potential distributions and the eventual failure of the cell. The addition of Zn to the electrolyte only accelerates this process, as ZnMn₂O₄ is even more electrochemically inert than Mn₃O₄. Local potential gradients can trigger this transformation at electrode-averaged depths of discharge as low as 20%, depending on the construction of the electrode.(11, 13) This is a major failure mode of all rechargeable cells that use MnO₂ as a cathode material, especially those using Zn as a counter electrode.(7)

Varying individual factors of the EMD microstructure, such as the Mn stoichiometry, surface area, or cation vacancy fraction has little to no impact on the long-term cyclability of the cell, as crystallographic changes produced by charging and discharging the cell dominate the system, leading to the loss of the EMD crystal structure after the first full cycle.(14) Alternative methods for developing alkaline cells with superior cyclability include MnO₂–C composites(15, 16) and doping MnO₂ with materials such as Bi, Ba, Ti, or Ni.(12, 17-20) The modified materials have increased depth of discharge, and Bi and Ba doped materials in particular have high performance. However, doping has yet to solve the problem of Zn poisoning; when cycled in an electrolyte containing zinc ions, doped cathodes still form electrochemically inactive hetaerolite.(21) Another approach used for the prevention of hetaerolite formation is the use of alternative electrolytes. To resolve the issue of hetaerolite formation, LiOH has been used instead of KOH in MnO₂–Zn cells. When a saturated LiOH electrolyte is used instead of KOH, discharge capacity retention of at least 50% is extended from as little as 2 cycles to more than 40. This enhancement in cyclability may be attributable to the alternate insertion mechanism: rather than forming MnOOH and Mn(OH)₂ via proton insertion, reduction of MnO₂ in a LiOH electrolyte results in lithium insertion, forming the Li_xMnO₂ (0 < x < 1) phase.(22) Without the formation of its precursor phase, MnOOH, the irreversible ZnMn₂O₄ phase is not formed. However, the cell capacity is substantially reduced, from ~325 to ~150 mAh/g. The reduced capacity of MnO₂ cycled in pure LiOH electrolyte is due to the limited insertion capacity for Li in the MnO₂ structure. At most, only 1 Li ion can be inserted into the structure, and due to the poor ionic conductivity of Li⁺ ions in MnO₂, full insertion is rarely achieved. As in primary cells, the addition of transition and alkali metal oxides, such as MgO, Bi₂O₃, or BaO, can substantially improve the capacity and cyclability of MnO₂–Zn aqueous Li-ion batteries, in part by reducing the crystallinity of the Li_xMnO₂ spinel and improving its ionic conductivity. However, none of these additives fundamentally change the insertion mechanism of the system, preventing proton insertion from occurring and limiting the maximum theoretical capacity of the cathode.(23-25)

In this work, a Bi₂O₃ in β-MnO₂ composite cathode material has been synthesized using a simple hydrothermal method and cycled in a mixed KOH–LiOH electrolyte with a range of concentrations. We show that, at a KOH:LiOH molar ratio of 1:3, both proton insertion and lithium insertion occur, allowing access to a higher fraction of the theoretical capacity of the MnO₂ while preventing the formation of ZnMn₂O₄. This enables a capacity of 360 mAh/g for over 60 cycles, with cycling limited more by anode properties than traditional cathodic failure mechanisms. The structural changes occurring during cycling are characterized using electron microscopy and in situ synchrotron energy-dispersive X-ray diffraction (EDXRD) techniques. This mixed electrolyte shows exceptional cyclability and capacity and can be used as a drop-in replacement for current alkaline batteries, potentially drastically improving their cycle life and creating a wide range of new applications for this energy storage technology.

MnO₂ Synthesis

Our active cathode material, a Bi₂O₃ in β-MnO₂ composite (MBDB), was prepared by a thermal decomposition process with a mixture consisting of Mn(NO₃)₂·4H₂O (Sigma-Aldrich, purum p.a., >97.0%), Bi(NO₃)₃·5H₂O (Sigma-Aldrich, ACS reagent grade, > 98.0%), and nitric acid

(Sigma-Aldrich, ACS reagent grade, 70%)

Two different solutions were prepared: (1) 50 g of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 80 mL of H_2O and (2) 4.27 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 18.6 mL of H_2O and 6.4 mL of HNO_3 . They were mixed separately first to ensure full dissolution of the precursors before being mixed together. The final solution was mixed using a magnetic stir-plate while heated by incrementally increasing the temperature with steps of 5 °C/min and an end temperature of 125 °C. The evolution of oxidation was visually observable through color changes of the solution. The end oxidation state (4+) resulted in a black solution, which was kept in vacuum at 125 °C overnight to ensure that all NO_x gases produced from the decomposition of nitric acid were eliminated. The sample was taken out after 12 h and baked at 325 °C for 5 h in a conventional oven. Finally, the dried and solid material was ground using mortar and pestle to break up the agglomerates of material. Our process for producing undoped $\beta\text{-MnO}_2$ (pyrolusite) was identical to our process for producing MBDB, but left out the bismuth nitrate pentahydrate from solution 2.

Electrochemical Techniques

After production of MBDB powder, the electrodes were mixed with conductive additives and Teflon emulsion (Sigma-Aldrich) and dried in a vacuum oven at 125 °C for 1 h. Two separate sets of additives were used: graphite (Timcal KS6) and carbon black (Timcal Super C). The electrodes made using graphite were 45% MBDB, 45% graphite, and 10% PTFE, while the electrodes made using carbon black were 60% MBDB, 30% CB, and 10% PTFE. After the electrodes were cast and dried, they were embedded onto a perforated Ni mesh and pressed using a pressure of 138 MPa to calendar the electrodes. The pressed electrodes were then assembled into planar cells, using acrylic plates held together with screws to maintain compression. The counter electrode was Zn metal plate. The separator used was 1 layer of polyvinyl chloride and 2 layers of nonwoven cellulose (FV-4304, Freudenberg LLC). The electrodes made using a mixture of MBDB and carbon black had an areal loading of 0.064 g/cm² and a total active mass per cell of 0.2 g. After assembly, the cells were immersed in a small sealed beaker of electrolyte containing 5 mL of electrolyte and cycled, either at a C/3 rate, a C/20 rate, or a C/4.2 rate, as described. Constant current rates were calculated with a MnO_2 capacity of 616 mAh/g. The voltage range used was $1.8 > V > 0.4$. At the end of constant current charging, a constant voltage of 1.8 V was applied until the current dropped to 10% of the maximum constant current value. The cells were cycled using a MTI BST8-3 battery analyzer.

Electrochemical impedance spectroscopy studies were carried out on these cells using an AC amplitude of 10 mV and a frequency range from 10 mHz to 10 kHz, using a Solartron 1260 frequency response analyzer. To obtain resistance and diffusion parameters, an equivalent circuit model was applied to EIS measurements, using a standard Randles circuit.⁽²⁶⁾ R_s represents the resistance of the cell, including electrolyte and ohmic impedance. R_{ct} represents the charge transfer resistance occurring at the surface of the electrode. The constant phase element (CPE) accounts for the double layer capacitance. Z_w represents the Warburg resistance from ionic diffusion in the MnO_2 bulk, which originates from the diffusivity of both protons and lithium ions in our case. The CPE is defined by two constraint parameters: CPE-T, the capacitance from an ideal double-layer capacitor, and CPE-P, a measurement of surface tortuosity.

SEM, XRD, and Surface Area Characterization

Scanning electron microscopy micrographs were produced using a Philips XL 30 environmental scanning electron microscope (ESEM), operated at an accelerating voltage of 20 kV. Ex-situ

XRD measurements were performed via powder diffraction XRD (pXRD) techniques, acquired using a Bruker D8 advanced diffractometer with a Bragg–Brentano θ – 2θ geometry and Cu K α source ($\lambda = 1.54$). The samples were scanned from 10 to 80 degree at a scan rate of 0.0125° s⁻¹. We used Brunauer–Emmett–Teller (BET) techniques to analyze the material, using a Micromeritics Instrument Corporation ASAP 2020 nitrogen sorption system. Our results showed that MBDB possessed a specific surface area of 23.9 m²/g.

EDXRD

A small beaker cell, printed using a Form 1 3D printer (Formlabs), was assembled. The printed photolithography resin was used because of its demonstrated base stability and X-ray transparency. The printed photolithography resin was confirmed to be of high X-ray transparency. The electrode was cycled under noncompression conditions in a 1 M KOH + 3 M LiOH electrolyte, against a Zn plate counter electrode. A C/4.2 rate was used, without an initial C/20 cycle. Cycling conditions were otherwise identical to those described previously. Constant current–constant voltage battery discharge was done using an MTI BST8-3 battery analyzer. EDXRD experiments were conducted at the National Synchrotron Light Source (NSLS) on the 7-pole superconducting wiggler beamline X17B1 at Brookhaven National Laboratory (BNL). During battery testing, an incident X-ray beam was fired at the battery being tested, and the diffracted beam was detected at a fixed angle $2\theta = 3^\circ$. The collimation slits were set to control the sizes of the incident and scattered beams, whereby the intersection of the two beam cross-sectional areas defined a gauge volume (GV). The careful positioning of the GV allowed diffraction data to be collected from a spatially well-defined location. The collimation slits were set for values of $d_i = 50\ \mu\text{m}$ and $d_s = 100\ \mu\text{m}$. This produces a GV with a flat parallelepiped shape: 50 μm in the x1-direction, approximately 1.4 mm in the x2-direction, and 2 mm in the x3-direction.⁽²⁷⁾ The battery was moved using an X-Y-Z stage to scan the GV across the cathode, collecting EDXRD data at 366 μm intervals, covering the thickness of the cell cathode with 3 individual scans. Data were collected at each point for 1 min as the cell was cycling. The incident beam was white beam radiation with an energy range of <20–200 keV. Attenuation of the beam while traveling through the cell was minimal above 50 keV, where diffraction data were analyzed. The EDXRD detector was a standard cryogenically cooled high-resolution Canberra intrinsic Ge detector. The cryostat was configured for operation in an inclined angle operation. The Ge single crystal of the EDXRD detector was 1 cm thick, in order to enhance high absorption efficiency of high energy X-rays (about 90% at 100 keV). The detector was mounted on the arm of a Huber diffractometer, with a lead-shielded diffraction beam path to attenuate extraneous X-rays scattered in the white beam radiation hutch.^(27, 28) A digital signal processor and an 8192-channel multichannel analyzer were used with the detector. X-ray energy calibration was performed using LaB6 and CeO2 standards.

XRD spectra and scanning electron micrographs of the synthesized MBDB powder are shown in Figure 2a and b. A Rietveld refinement was conducted in order to elucidate the structure of the material and to better estimate the Bi:Mn stoichiometry. The refinement was performed using FullProf software. From Figure 2a, the peaks at 31–34° are attributed to a Bi₂O₃ diffraction (ICSD 417638) while the rest of the peaks are well matched with β -MnO₂ (ICSD 73716). The Bi₂O₃ peaks region (31–34°) is excluded to get a more precise refinement fit. These results showed that bismuth atoms replaced 3.5% of the manganese atoms in the (0,0,0) position. The oxygen atom is located at (0.3046, 0.3046, 0), and has occupancy of 2, with Rp and Rwp values

of 9.8 and 15.4, respectively. The micrograph image (Figure 2b) indicates that the MBDB powder consists of agglomerated particles in a 50–100 nm diameter range. These results show that our synthesis method was able to produce a MBDB powder with a small particle size and with a Bi_2O_3 well distributed in a $\beta\text{-MnO}_2$. Although $\beta\text{-MnO}_2$ is often considered an electrochemically inactive phase, electrochemical activity is primarily governed by cation vacancies, which facilitate proton transport. It has previously been demonstrated that highly crystalline materials with few defects exhibit poor electrochemical activity regardless of their phase, and that proton transport can be facilitated either by the mixture of pyrolusite layers into the ramsdellite structure or by other defect types such as microtwinning. The MBDB produced via our method is highly defective, with accordingly increased electrochemical activity.(10)

Figure 2. (a) Ex situ XRD spectra of MBDB, including as-scanned (black), the model produced by Rietveld Refinement (red), ICSD peak positions for pyrolusite (green), and the difference between as-scanned and model (blue), and (b) scanning electronic microscopy image (SEM).

Mixed electrolytes made up of a mixture of KOH and LiOH in a wide composition range, from 4 M KOH to 4 M LiOH, were tested at a C/3 rate. Subsequently, a second set of tests was performed in a more narrow composition range with slower rates, initially discharging and charging the cell at a C/20 rate for the first cycle, and subsequently charging it at a C/4.2 rate. These results are shown in Figure 3a and 3b, respectively.

Figure 3. MBDB cells cycled at a (a) C/3 rate and (b) C/20 rate for the first cycle and C/4.2 rate for subsequent cycles against Zn plate in a range of different electrolytes. (c) MBDB cycled in 1 M KOH + 3 M LiOH at a C/20 rate for the first cycle and C/4.2 rate on subsequent cycles, demonstrating the effect of different conductive additives, carbon black and graphite, on capacity. (d) Coulombic efficiency of MBDB vs Zn cells in a range of electrolytes and different conductive materials.

When cycled at a C/3 rate, the 4 M KOH, 3 M KOH + 1 M LiOH, and 2 M KOH + 2 M LiOH cells show a similar pattern of behavior, with a rapid and exponential decline in capacity from an initial value of ~ 350 to ~ 75 mAh/g. The 1 M KOH + 3 M LiOH and 4 M LiOH cells, however, show a much smaller drop in capacity with cycling. The 4 M LiOH cell fails relatively rapidly due to passivation of the Zn plate, however, as the ZnO passivating film cannot dissolve well in a weak base such as LiOH.(29) The 1 M KOH + 3 M LiOH cell shows a capacity over 100 mAh/g for more than 50 cycles with relatively little fading after the first cycle. Subsequent tests at slower rates in a narrower composition range, shown in Figure 3b, demonstrate that the superior performance seen in the 1 M KOH + 3 M LiOH electrolyte cell is localized to a composition range of approximately 1:3 to 3:7 KOH:LiOH. Within this composition range, we see relatively high capacity, with a peak value of ~ 280 mAh/g. If the KOH:LiOH ratio is reduced to 1:4 or increased to 1:2, a dramatic loss of capacity occurs, reducing performance to ~ 125 –75 mAh/g

after the first cycle. This is presumably due to either the loss of the proton insertion mechanism for charge storage (when the KOH:LiOH ratio is reduced) or the development of electrochemically inactive heterolite (when the KOH:LiOH ratio is increased).

To further improve performance, we replaced the graphite conductive additive used in our electrodes with carbon black, a higher surface area conductive additive. These results are shown in Figure 3c. Carbon black is noted to improve overall performance in MnO₂ cathodes undergoing deep discharge by reducing the size of the product phase particles and enhancing overall electrode conductivity, at the cost of open circuit potential.(30, 31) As predicted, cells assembled with carbon black instead of graphite exhibited ~200 mV lower open circuit potential, due to the interaction of the surface groups on the carbon black with the MnO₂. However, the higher surface area of the amorphous carbon significantly enhances interdigitation of the conductive additives and active material, leading to a substantial improvement of the overall capacity of the full cell, increasing capacity from ~280 to ~360 mAh/g. This is accomplished without reducing the average potential of discharge; instead, a larger fraction of the electrode capacity is accessible. The capacity of these cells is high enough that performance cannot be explained only by lithium insertion into the MnO₂. The maximum capacity of lithiated MnO₂, for a full first electron reduction to LiMnO₂, is 285 mAh/g. After ~60 cycles, the cell fails due to the complete dissolution of the Zn anode.

The impact of the electrolyte and conductive additives on Coulombic efficiency was also examined, as shown in Figure 3d. After the first cycle, the efficiency of every cell is over 80%. The high Coulombic efficiency after the initial capacity fade indicates that critical capacity fade mechanisms are stabilized in all cases, but that the electrolyte mix determines the extent of critical fade. Cells with higher capacity, such as those made with carbon black conductive additives, tend to exhibit lower efficiency, although once cell break-in is completed, the efficiency increases to ~95%. Cells made with graphite conductive additives exhibit Coulombic efficiency of ~99%. The reduced Coulombic efficiency of the cells made with carbon black conductive additives may be due to the poor oxidative stability of amorphous carbon as compared to that of graphite.

To better understand the impact of both the bismuth dopants and the mixed electrolyte on the phase transformation occurring in the cathode, we performed a careful galvanostatic analysis of the first discharge of MnO₂ cycled with Bi₂O₃ composite (MBDB) and without (pyrolusite) and in both pure KOH and 1 M KOH + 3 M LiOH electrolytes. These results are shown in Figure 4. Our results show that the second electron discharge regions of the bismuth-doped cells are much larger than those of the undoped cells, and tend to occur at a lower reduction potential. This is likely due to the fact that bismuth acts as a redox catalyst, stabilizing the structure and extending the discharge regime.(32) In addition, the presence of bismuth in the structure may promote the formation of Bi–Mn complexes, which inhibit the formation of undesirable products, such as Mn₃O₄; this may in turn enhance the overall capacity and retention of the cell.(20) Mn³⁺ is known to dissolve into electrolyte and be reduced to Mn²⁺. These two dissolved species tend to react with each other, however, and produce Mn₃O₄. The presence of bismuth in the structure enables it to dissolve into electrolyte and become the positively charged complex Bi₆(OH)₁₂⁶⁺. This compound is known to combine with Mn(OH)₂^{3–} or Mn(OH)₂^{4–}, forming Bi–Mn complexes, and thereby inhibiting the formation of the lower-cyclability Mn₃O₄ phase.(33–36) This may explain why a flatter and longer voltage profile regime is present in bi-doped samples, and why they generate higher capacity.(32) Figure 4b also shows that cells cycled in the 1 M

KOH + 3 M LiOH electrolyte exhibit a less distinct separation between the first- and second-electron discharge plateaus, presumably due to the simultaneous insertion of lithium into the structure providing a secondary reduction mechanism.

Figure 4. Comparison of the pyrolusite and MBDB cells with 4 M KOH or 1 M KOH+ 3 M LiOH cells, cycled at a C/3 rate in a three-electrode configuration against Hg/HgO reference electrode (+0.098 V vs SHE). (a) Specific discharge capacity vs cycle index; (b) discharge potential vs specific discharge capacity.

These results indicate that the use of a mixed electrolyte with precisely balanced KOH:LiOH ratio can dramatically enhance the overall cyclability of a MnO₂-Zn cell. To elucidate the effects of this mixed electrolyte on the microstructural changes occurring within the MBDB cathode, EDXRD was performed on a small-scale cell. This in situ study was performed at the X17B beamline at the National Synchrotron Light Source at Brookhaven National Laboratory, the results of which are shown below in Figure 5.

Figure 5. In situ EDXRD studies on a MBDB cell with graphite conductive additives cycled against zinc metal in 1 M KOH + 3 M LiOH. The colored vertical arrows indicate peaks associated with particular phases; the black horizontal arrows at right indicate the end of a specific charge or discharge stage of the MBDB electrode.

Our in situ studies showed that the MBDB is fully reduced to Mn(OH)₂, with peaks apparent at 81.42, 95.2, 128.5, and 141.4 keV. This confirms that proton insertion occurs in the electrode despite the presence of lithium ions. However, the increase in intensity during discharge of the peak at 77.8 keV suggests that LiMn₂O₄ is also present. The presence of both product phases simultaneously suggests that lithium and proton insertion occur simultaneously during reduction of the cathode. During reoxidation of the cathode, the MBDB structure that the electrode originally possessed is not recovered. In fact, within the range of photon energies scanned, no crystalline manganese oxide phases are present when the electrode is charged.

Conventional, ex situ XRD techniques were also carried out to characterize the cells with carbon black conductive additives at fully discharged (−1 V vs Hg/HgO) and fully recharged (+0.3 V vs Hg/HgO) states. The results are shown in Figure 6A.

Figure 6. (A) Ex situ XRD patterns of structural evolution of the MBDB composite electrodes with carbon black conductive additives in 1 M KOH + 3 M LiOH at various states of discharge: (a) MBDB pristine powder, (b) MBDB pristine electrode, (c) after full discharge of the 1st cycle, and (d) after full recharge of 1st cycle. (B) High-resolution scanning electron microscopy (SEM) micrographs showing the microstructural change for MBDB electrodes cycled in 1 M KOH + 3

M LiOH after full recharge.

As shown in the EDXRD results, when the electrode is fully discharged, a strong peak appears at 19° , equivalent to the peak at 77.8 keV in Figure 5, indicated the presence of LiMn_2O_4 . The presence of $\text{Mn}(\text{OH})_2$ is similarly indicated. For the fully recharged sample, however, a significant peak appears at 12° . The peak at this angle can be assigned to the birnessite family.(37) The resulting dramatic physical transformation, shown in Figure 6B, confirms an extensive change in the microstructure of the material after cycling. The absence of birnessite in Figure 5 is a product of the limited energy range of the EDXRD scan. On the basis of this information, we have included in Figure 7 a schematic of our best estimate of the structural transformations occurring in the MBDB material when cycled in 1 M KOH + 3 M LiOH.

Figure 7. Proposed phase transformation of MBDB cell under KOH:LiOH = 1:3 electrolytes.

As shown in Figure 7, the cathode is, in the first cycle, converted into a mixture of LiMn_2O_4 and $\text{Mn}(\text{OH})_2$ at the fully discharged state when the 1 M KOH + 3 M LiOH electrolyte is used. This is followed by a transformation to the layered birnessite structure at the fully recharged state. The (111), (113), and (222) LiMn_2O_4 peaks, at 19.1 , 33.9 , and 44.9° respectively, continue to be visible in the fully recharged state, albeit at diminished relative intensity. This suggests that Li extraction from the cathode is not fully completed, presumably due to slow diffusion of Li through the spinel structure. This reaction is frequently considered rate-limiting in aqueous Li-ion cells. However, the partial extraction of lithium from the spinel phase will minimize the development of Jahn–Teller distortion, which may be caused by the presence of the spinel phase.(38) The absence of intermediate Mn^{3+} oxides, such as MnOOH or Mn_2O_3 (see Figure 1), may be explained by the simultaneous first- and second-electron reduction of the cathode.(11, 39) We hypothesize that the exclusion of the intermediate Mn^{3+} phases formed during normal proton insertion in favor of lithiated Mn spinel phases is key to the role of the 1 M KOH + 3 M LiOH electrolyte in improving cyclability. The irreversible ZnMn_2O_4 phase is produced by reaction of these intermediates with solvated zincate ions.(11) The concentration of KOH is still high enough for a full second electron reduction of the MnO_2 to occur, resulting in the formation of $\text{Mn}(\text{OH})_2$, but the protonated intermediates do not form. By contrast, when cycled in pure KOH, the irreversible phases ZnMn_2O_4 and Mn_3O_4 form in addition to $\text{Mn}(\text{OH})_2$. While $\text{Mn}(\text{OH})_2$ can be oxidized to birnessite, these irreversible phases cannot. Consequently, the fraction of irreversible products increases with each subsequent cycle. These results are further supported by the SEM images shown in Figure 8, in which the MBDB cathode is shown before cycling, in the fully discharged state (-1 V vs Hg/HgO), and in the fully recharged state ($+0.3$ V vs Hg/HgO).

Figure 8. Scanning electron microscopy (SEM) micrographs demonstrating the change of morphology for MBDB electrodes with 4 M KOH electrolyte (a) after first cycle discharge, (b) after first cycle recharge, (c) after tenth cycle fully discharged, and with 1 M KOH + 3 M LiOH electrolyte (d) after first cycle discharge, (e) after first cycle recharge, (f) after tenth cycle fully discharged.

For the cell with 1 M KOH + 3 M LiOH, in the fully discharged state, the electrode is highly homogeneous, with 1- μ m rounded particles of manganese-hydroxide-coated carbon black. During discharge, manganese dissolves and reprecipitates onto the conductive additives in the electrode as part of the $\text{Mn}^{3+}/\text{Mn}^{2+}$ reduction, with the size of the product particles being limited by the electrical conductivity of the product phase. A similar effect occurs during the oxidation of the cathode active material.(36) When the electrode is recharged, the electrode appears to be mostly composed of rounded, small particles with a diameter of around 50 nm, which appear to be highly agglomerated. After 10 cycles in the fully discharged state, the particle size is reduced to 20-nm diameter, with a more discrete morphology. However, when the cell is cycled with only KOH as an electrolyte, the electrode is no longer homogeneous in the discharged state. Instead, large hexagonal particles with a 5- μ m diameter are produced, coupled with much smaller, $\sim$ 50 nm rounded particles. This is a radical change from the initial structure of the MBDB particles, as seen in Figure 2b. After subsequent oxidation of the electrode, larger agglomerated particles begin to form, creating void spaces in the previous contiguous electrode. By the tenth cycle, these agglomerated particles of electrochemically inactive material, presumably ZnMn_2O_4 , take up a significant fraction of the electrode volume. The combination of the formation of inactive phases and physical disruption of the electrode may both contribute to the capacity fading of the cell. The microstructural and morphological changes of the MBDB cell cycled in 1 M KOH + 3 M LiOH is much more homogeneous than the pure KOH cell, which may be a factor in the superior capacity retention of the mixed electrolyte. The more homogeneous morphological changes result in the decrease of formation of cracks and holes formation in the electrode, which may also enhance cycle life for the cell. The electrodes shown in Figure 8 were also studied via energy-dispersive X-ray spectroscopy (EDX). The electrode cycled in 4 M KOH showed a significant quantity of Zn, with a Zn:Mn atomic ratio of 1:8.11. This suggests that as much as $\sim$ 24.7% of the MnO_2 in the electrode has been converted into ZnMn_2O_4 . However, the cell cycled in 1 M KOH + 3 M LiOH showed no Zn present, suggesting that the formation of ZnMn_2O_4 had been completely averted.

We have also characterized the electrochemical impedance parameters of the MnO_2 -Zn cell in order to understand its electrical properties. Electrochemical impedance spectroscopy (EIS) measurements were performed with three-electrode cell configurations, the results of which are shown in Figure 9.(26) The results were fitted to a standard Randles circuit to derive the electrochemical impedance characteristics of this system, which are shown in Table 1.

Figure 9. Electrochemistry impedance spectroscopy (EIS) analysis of a MBDB vs Zn cell in both KOH and 1 M KOH + 3 M LiOH conditions before the first cycle and after the tenth cycle.

Table 1. Fitting Parameters of the EIS Analysis Obtained from the Equivalent Circuit Model

sample ID	state	Rs (Ω)	Rct (Ω)	W1 (Ω s ^{-1/2})	CPeI (F s ^{a-1})
MBDB - 4M KOH	as prepared	0.029	0.183	0.287	0.0330 (a = 0.684)
MBDB - 4M KOH	10th cycle	0.068	0.583	0.580	0.0019 (a = 0.877)
MBDB - 1 M KOH + 3 M LiOH	as prepared	0.054	0.544	0.646	0.0021 (a = 0.871)
MBDB - 1 M KOH + 3 M LiOH	10th cycle	0.034	0.538	0.688	0.0016 (a = 0.897)

The fitting parameters for our EIS results are shown in Table 1. When MnO₂ is cycled in 1 M KOH + 3 M LiOH instead of 4 M KOH, the Ohmic impedance (Rs), double-layer capacitance (Cdl), and charge transfer impedance (Rct) are all significantly increased. This suggests that a different reduction reaction, presumably Li insertion, is rate-limiting in cells using a mixed electrolyte rather than pure KOH. As a result, the Mn⁴⁺/Mn³⁺ redox couple is dominated by the process of Li insertion, rather than proton insertion, as is the case in EMD (see Figure 1). Changes in Rs and Rct after cycling also are significantly impacted by our choice of electrolyte. Rs and Rct for the MBDB cell in 1 M KOH + 3 M LiOH electrolyte are slightly smaller at the tenth cycle than in their initial state, suggesting that the surface properties of the electrode do not change significantly with cycling, and the overall shape of the Nyquist plot is quite similar for both points in the cell lifetime. The cell cycled with 4 M KOH showed lower Rct in the pristine state than the cell with 1 M KOH+3 M LiOH, but by the tenth cycle, the Rct is substantially higher than that of the cell in its pristine state. This result may be correlated to the microstructural changes previously described, as much of the cell has been converted into an electrochemically irreversible and inert phase.

A study on the impact of mixed mixtures of KOH and LiOH electrolytes in MnO₂-Zn cells has been undertaken. It was found that, depending on the exact composition of the electrolytes, either proton insertion, lithium insertion, or a combination of both mechanisms can dominate the reduction of the MnO₂. When lithium insertion or combined lithium-proton insertion is the

dominant reduction mechanism, zinc poisoning reactions do not occur, allowing much greater cycle lifetimes for the cell: up to 60 cycles with minimal loss of capacity, limited primarily by the dissolution or passivation of our Zn plate anode. At the correct electrolyte composition, consisting of 1 M KOH and 3 M LiOH, both lithium and proton insertion mechanisms occur, enabling full two-electron reduction of the MnO₂. We have analyzed the structural and microstructural changes occurring in the electrode using a variety of techniques, including in situ EDXRD, conventional ex-situ XRD, and scanning electron microscopy techniques. We have concluded that this improvement in cyclability is due to the exclusion of intermediate protonated Mn³⁺ phases produced during normal proton insertion in favor of lithiated Mn spinel phases that are not susceptible to Zn poisoning. We have also analyzed the role of bismuth in the cathode material, concluding that bismuth acts as a redox catalyst, stabilizing the structure and extending the second-electron discharge regime. With appropriate cycling protocols and additives, the capacity of the MnO₂ cathode is increased dramatically, up to as much as 360 mAh/g. Because of the high capacity of the MnO₂–Zn cell, the theoretical energy density of a rechargeable alkaline cell could be as high as 100–150 Wh/kg, with extremely low material costs and exceptional safety compared to other rechargeable battery technologies (probably less than 60\$ per kilowatt hour). Rechargeable alkaline batteries using mixed electrolytes show significant potential for a sustainable energy storage solution in the fields of grid storage and electric vehicles.

#Author Contributions

Authors B.J.H. and A.H. equally contributed.

The authors declare no competing financial interest.

Acknowledgment

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Manganese dioxide electrode. 1V. Chemical and electrochemical reduction of an electrolytic γ -manganese dioxide

Maskell, W. C.; Shaw, J. E. A.; Tye, F. L.

Electrochimica Acta (1981), 26 (10), 1403-10 CODEN: ELCAAV; ISSN:0013-4686.

The chem. or electrochem. redn. of γ -MnO₂ proceeds via a single phase over the complete range MnO₂-MnO_{1.5}. The end member MnO_{1.5} was named δ -MnOOH to distinguish it clearly from groutite. If the de Wolff model for γ -MnO₂ is accepted, then δ -MnOOH is an intergrowth structure of groutite with microdomains of manganite. The oxyhydroxide is metastable in the region MnO_{1.75}-MnO_{1.5}, slowly pptg. γ -MnOOH as a sep. phase in aq. solns., probably by a dissoln.-pptn. mechanism. The filling of the lattice with electrons and protons appears to proceed differently in the ranges MnO₂-MnO_{1.75} and MnO_{1.75}-MnO_{1.5}. Two ways in which this might come about are proposed. Evidence from Jahn-Teller distortion favors the explanation that in the 1st half of redn. an electron entering the structure is delocalized between 2 adjacent Mn⁴⁺; in the 2nd half an added electron displaces a shared electron and the 2 electrons are assocd. with individual cations forming Mn³⁺.

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Alkaline manganese dioxide electrode. I. The discharge process

Boden, David P.; Venuto, C. J.; Wisler, D.; Wylie, R. B.

Journal of the Electrochemical Society (1967), 114 (5), 415-17 CODEN: JESOAN; ISSN:0013-4651.

The cathodic redn. of γ -MnO₂ in alk. electrolyte was studied by examn. of const. current discharge curves, by x-ray diffraction, and by chem. analysis. The reaction takes place by a 3-step process whereby an amorphous intermediate is formed by assimilation of protons in the γ -MnO₂ lattice. As redn. proceeds, the intermediate crystallized to give Mn₃O₄ and finally Mn(OH)₂, depending on the electrode potential. The rapid increase in electrode resistance at approx. half of the capacity is related to the formation of interfacial films of Mn₃O₄.

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[CrossRef], [CAS]

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Electrochemistry of β - and γ -manganese dioxide in alkaline electrolyte

McBreen, James

Electrochimica Acta (1975), 20 (3), 221-5 CODEN: ELCAAV; ISSN:0013-4686.

The electrochem. reactions of β -MnO₂ [1313-13-9] and γ -MnO₂ in 7 M KOH was studied using low-rate linear sweep voltammetry (≈ 25 μ V/sec) in conjunction with x-ray anal. of the reaction products. The redn. of β -MnO₂ differs from γ -MnO₂ in that there is no dilation of the β -MnO₂ crystal lattice and Mn₃O₄ [12502-70-4] (hausmannite [1309-55-3]) is formed. The irreversibility of γ -MnO₂ electrodes is related to the formation of Mn(OH)₂. Mn(OH)₂ is oxidized to δ -MnO₂ and δ -MnO₂ forms Mn₃O₄ on redn. Hausmannite resists electrochem. oxidn. Poorly crystallized γ -MnOOH is formed as an intermediate in the oxidn. of Mn(OH)₂ to δ -MnO₂. The formation of Mn₃O₄ is discussed in terms of the potential-pH diagram for Mn oxides and the thermodyn. properties of MnOOH.

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Rechargeable alkaline manganese dioxide batteries. I. In situ x-ray diffraction investigation of

the hydrogen ion(+)/ γ -manganese dioxide (EMD-type) insertion system

Mondoloni, Christian; Laborde, Marc; Rioux, Jacques; Andoni, Edouard; Levy-Clement, Claude
Journal of the Electrochemical Society (1992), 139 (4), 954-9 CODEN: JESOAN; ISSN:0013-4651.

The electrochem. insertion and deinsertion of H^+ was investigated by studying its influence on the evolution of the crystallog. structure of γ - MnO_2 of EMD type (electrochem. method deposition) during the discharge and recharge processes of an alk. battery, using in situ x-ray diffraction. During the first discharge, proton insertion up to $X = 0.4 H^+$ per MnO_2 with concomitant electron transfer causes an expansion of the MnO_2 cryst. cell. The lattice expansion is attributed to the redn. of Mn^{4+} ions to Mn^{3+} ions which have a larger ionic radius. Between 0.5 to 0.8 H^+ inserted the long-range order is lost and the presence of a quasi-amorphous phase which could not be identified is detected. This amorphous phase is reduced to γ - Mn_2O_3 (or Mn_3O_4) and to $Mn(OH)_2$ when more than 0.8 H^+ is inserted. On recharge, the $Mn(OH)_2$ is oxidized to γ - Mn_2O_3 (or Mn_3O_4) leading to poor cycling of the battery. When the discharge is limited to 0.8 H^+ the battery can be recharged and cycled many times. Still more cycles can be obtained when the discharge is limited to 0.5 H^+ , corresponding to the range where the γ - MnO_2 structure is retained. In this range, strong hysteresis in the voltage curves indicated that while there is structural reversibility, structural changes arise at different voltages on discharge and recharge.

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Van der Ven, A.; Morgan, D.; Meng, Y. S.; Ceder, G. Phase Stability of Nickel Hydroxides and Oxyhydroxides J. Electrochem. Soc. 2006, 153 (2) A210– A215, DOI: 10.1149/1.2138572

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Phase Stability of Nickel Hydroxides and Oxyhydroxides

Van der Ven, A.; Morgan, D.; Meng, Y. S.; Ceder, G.

Journal of the Electrochemical Society (2006), 153 (2), A210-A215 CODEN: JESOAN; ISSN:0013-4651. (Electrochemical Society)

The authors study phase stability of several Ni hydroxides from 1st-principles. Hydrogen removal from β - $Ni(OH)_2$ is predicted to occur through a biphasic reaction to β - $NiOOH$ involving a change in the stacking sequence from T1 [for β - $Ni(OH)_2$] to P3 (for β - $NiOOH$). Further topotactic removal of hydrogen from β - $NiOOH$ can only occur after a step at 0.4-0.9 V is surpassed. The authors also propose an energetically stable crystal structure for stoichiometric γ - $NiOOH$, which offers an explanation for the oxidn. limit of 3.66 for Ni. In this structure, K in the intercalation layer resides halfway between adjacent trigonal prismatic sites. The authors conclude with a discussion of the role of the electrolyte in detg. phase stability as well as the

voltage profile of γ -NiOOH.

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Devaraj, S.; Munichandraiah, N. Effect of Crystallographic Structure of MnO₂ on Its Electrochemical Capacitance Properties J. Phys. Chem. C 2008, 112 (11) 4406– 4417, DOI: 10.1021/jp7108785

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Effect of Crystallographic Structure of MnO₂ on Its Electrochemical Capacitance Properties

Devaraj, S.; Munichandraiah, N.

Journal of Physical Chemistry C (2008), 112 (11), 4406-4417 CODEN: JPCCCK; ISSN:1932-7447. (American Chemical Society)

MnO₂ is currently under extensive investigations for its capacitance properties. MnO₂ crystallizes into several crystallog. structures, namely, α , β , γ , δ , and λ structures. Because these structures differ in the way MnO₆ octahedra are interlinked, they possess tunnels or interlayers with gaps of different magnitudes. Because capacitance properties are due to intercalation/deintercalation of protons or cations in MnO₂, only some crystallog. structures, which possess sufficient gaps to accommodate these ions, are expected to be useful for capacitance studies. In order to examine the dependence of capacitance on crystal structure, the present study involves prepn. of these various crystal phases of MnO₂ in nanodimensions and to evaluate their capacitance properties. Results of α -MnO₂ prepd. by a microemulsion route (α -MnO₂(m)) are also used for comparison. Spherical particles of about 50 nm, nanorods of 30-50 nm in diam., or interlocked fibers of 10-20 nm in diams. are formed, which depend on the crystal structure and the method of prepn. The specific capacitance (SC) measured for MnO₂ is found to depend strongly on the crystallog. structure, and it decreases in the following order: α (m) > α equiv. δ > γ > λ > β . A SC value of 297 F g⁻¹ is obtained for α -MnO₂(m), whereas it is 9 F g⁻¹ for β -MnO₂. A wide ($\sim$ 4.6 Å) tunnel size and large surface area of α -MnO₂(m) are ascribed as

favorable factors for its high SC. A large interlayer sepn. ($\sim 7 \text{ \AA}$) also facilitates insertion of cations in $\delta\text{-MnO}_2$ resulting in a SC close to 236 F g⁻¹. A narrow tunnel size (1.89 $\text{\AA}$) does not allow intercalation of cations into $\beta\text{-MnO}_2$. As a result, it provides a very small SC.

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Hetaerolite Profiles in Alkaline Batteries Measured by High Energy EDXRD

Gallaway, Joshua W.; Menard, Melissa; Hertzberg, Benjamin; Zhong, Zhong; Croft, Mark; Sviridov, Lev A.; Turney, Damon E.; Banerjee, Sanjoy; Steingart, Daniel A.; Erdonmez, Can K.

Journal of the Electrochemical Society (2015), 162 (1), A162-A168 CODEN: JESOAN; ISSN:0013-4651. (Electrochemical Society)

Energy dispersive x-ray diffraction (EDXRD) with photons of high energy and high flux was used to map cryst. discharge products within alk. AA cells following discharge at various rates: C/160, C/80, C/40, C/20, C/10, and C/5. During the study, the sealed cells are never opened and thus never exposed to air. The technique's resolu. allows the various Mn oxide discharge products to be distinguished, which has previously proven difficult. In particular, colocalized Mn_3O_4 (hausmannite) and ZnMn_2O_4 (hetaerolite) phases are resolved at C/160, C/80, and C/40 rates. Following more rapid discharge at C/20, no hausmannite is obsd.: instead, two well-defined zones result, one consisting only of hetaerolite, and the other only of $\alpha\text{-MnOOH}$ (groutite), with a small transition region where both phases are detected. Modeling suggests the obsd. hetaerolite-groutite boundary positions are consistent with hetaerolite formation in regions of greater active material use. Radial hetaerolite and hausmannite profiles are calcd. and are a function of the discharge current, which also det. discharge capacity. Results also show formation of a $\alpha\text{-MnOOH}$ phase from oxidn. states $\text{MnO}_{1.7}$ to $\text{MnO}_{1.53}$ with relatively little $\gamma\text{-MnOOH}$ character.

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Im, D.; Manthiram, A. Role of Bismuth and Factors Influencing the Formation of Mn_3O_4 in

Rechargeable Alkaline Batteries Based on Bismuth-Containing Manganese Oxides J. Electrochem. Soc. 2003, 150 (1) A68– A73, DOI: 10.1149/1.1524611

[CrossRef], [CAS]

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Role of bismuth and factors influencing the formation of Mn₃O₄ in rechargeable alkaline batteries based on bismuth-containing manganese oxides

Im, D.; Manthiram, A.

Journal of the Electrochemical Society (2003), 150 (1), A68-A73 CODEN: JESOAN; ISSN:0013-4651. (Electrochemical Society)

The two-electron redn./oxidn. reactions of manganese oxide in alk. electrolytes have been investigated in the presence and absence of bismuth oxide by both galvanostatic discharge/charge and linear sweep voltammetry followed by examg. the products with X-ray diffraction. Although the presence of bismuth helps the formation of birnessite MnO₂, it could not completely prevent the formation of Mn₃O₄. However, the formation of Mn₃O₄ could be suppressed by controlling the scan rate during linear sweep voltammetry and/or the microstructure of the electrode. Mn₃O₄ appears to be formed by a chem. reaction between dissolved Mn(II) and Mn(III) complexes (intermediates) that have diffused away from the conductive path (graphite). Both a faster scan rate (discharge/charge rate) and an intimate mixing of the manganese oxide with graphite achieved by ball milling suppress the formation of Mn₃O₄ independent of the presence of bismuth.

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Dzieciuch, M. A.; Gupta, N.; Wroblowa, H. S.Rechargeable Cells with Modified MnO₂ Cathodes J. Electrochem. Soc. 1988, 135 (10) 2415– 2418, DOI: 10.1149/1.2095349

[CrossRef], [CAS]

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Rechargeable cells with modified manganese dioxide cathodes

Dzieciuch, M. A.; Gupta, N.; Wroblowa, H. S.

Journal of the Electrochemical Society (1988), 135 (10), 2415-8 CODEN: JESOAN; ISSN:0013-4651.

As opposed to Fe anode which does not affect the longevity and capacity retention of the modified MnO₂ cathodes in a battery, Zn has a deteriorating effect on the modified MnO₂ material due to the formation of hetaerolite at the cathode. Methods to alleviate this effect and produce viable modified MnO₂/Zn batteries are described. Two types of modified materials were used: an inhouse-synthesized Bi birnessite and a Bi₂O₃-doped γ -MnO₂ International Common Sample. At present these systems retain ~50% of their theor. 1-electron capacity even after 200

fast charge-discharge cycles.

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Bailey, M. R.; Donne, S. W. Structural Effects on the Cyclability of the Alkaline γ -MnO₂ Electrode *Electrochim. Acta* 2011, 56 (14) 5037– 5045, DOI: 10.1016/j.electacta.2011.03.095

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Structural effects on the cyclability of the alkaline γ -MnO₂ electrode

Bailey, Mark R.; Donne, Scott W.

Electrochimica Acta (2011), 56 (14), 5037-5045 CODEN: ELCAAV; ISSN:0013-4686. (Elsevier Ltd.)

The cyclability of Mn dioxide samples with a wide range of initial properties was studied using electrochem. methods. Cycling revealed that a common change occurs in all materials irresp. of initial properties, with the discharge behavior standardized by the tenth cycle. Modeling of the discharge behavior revealed the steady decline in the capacity with cycling can primarily be assigned to lower potential pyrolusite domains. Also, an examn. of chem. reduced and reoxidized γ -MnO₂ revealed an irreversible expansion of the γ -MnO₂ lattice upon redn. arising from localized buckling of the O framework.

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[CrossRef], [CAS]

15.

MnOx/C composites as electrode materials. I. Synthesis, XRD and cyclic voltammetric investigation

Bezdička, Petr; Grygar, Tomas; Klapšte, Bretislav; Vondrak, Jiri

Electrochimica Acta (1999), 45 (6), 913-920 CODEN: ELCAAV; ISSN:0013-4686. (Elsevier Science Ltd.)

MnOx/C composite material was obtained by pptn. on suspended carbon black particles from

dissolved KMnO_4 . Doped composites were obtained by addn. of Ca, Mg, Ni and other ions to the reaction mixt. The resulting solids are XRD amorphous or very poorly cryst., but their chem. compn., Mn valence and electrochem. behavior are very similar to those reported for birnessite, 7-A layered manganate(III,IV). The authors tested the electrochem. redn./oxidn. of the composite in 2M KOH using cyclic voltammetry with three kinds of electrodes: microparticles immobilized on a carbon electrode (voltammetry of microparticles, vmp), carbon paste electrodes (cpee) and PTFE-bonded electrodes (tbe). Each technique was used for its own merit: vmp is the best pilot technique, cpee enables fast quantification of the charge/mass relations, and tbe is the most reliable, but the slowest and the most laborious one. All the employed techniques yield directly comparable results. The composite can be discharged/recharged several tens of times at ~ 1 e-/Mn efficiency.

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16.

Huang, X.; Yue, H.; Attia, A.; Yang, Y. Preparation and Properties of Manganese Oxide/Carbon Composites by Reduction of Potassium Permanganate with Acetylene Black J. Electrochem. Soc. 2007, 154 (1) A26– A33, DOI: 10.1149/1.2388741

[CrossRef], [CAS]

16.

Preparation and Properties of Manganese Oxide/Carbon Composites by Reduction of Potassium Permanganate with Acetylene Black

Huang, Xingkang; Yue, Hongjun; Attia, Adel; Yang, Yong

Journal of the Electrochemical Society (2007), 154 (1), A26-A33 CODEN: JESOAN; ISSN:0013-4651. (Electrochemical Society)

Amorphous Mn oxide/C composites were synthesized by directly reducing K permanganate with acetylene black, a cheap reducing agent. A reaction is postulated and confirmed by checking the evolved CO_2 and other species such as CO_2 -3 and HCO_3^- in the mother liquor. All the composites were characterized by SEM, XRD and TG/DTA techniques. The electrochem. performance of the composites was also studied and one compn. delivered a discharge capacity ≤ 231 mA-h/g (1.14 Li/Mn) at a c.d. of 40 mA/g with good electrochem. performance at high rates. The results suggested that the reaction is suitable for prepg. a composite cathode material and these composite materials can be developed as cathode materials for rechargeable high-power Li batteries. Intercryst. H_2O which affects the behavior of the composites is also discussed.

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17.

Hertzberg, B.; Sviridov, L.; Stach, E. A.; Gupta, T.; Steingart, D.A Manganese-Doped Barium Carbonate Cathode for Alkaline Batteries J. Electrochem. Soc. 2014, 161 (6) A835– A840, DOI: 10.1149/2.083405jes

[CrossRef], [CAS]

17.

A Manganese-Doped Barium Carbonate Cathode for Alkaline Batteries

Hertzberg, Benjamin; Sviridov, Lev; Stach, Eric A.; Gupta, Tanya; Steingart, Daniel

Journal of the Electrochemical Society (2014), 161 (6), A835-A840 CODEN: JESOAN; ISSN:0013-4651. (Electrochemical Society)

MnO₂-Zn alk. batteries are one of the most common modern forms of primary battery, due to their relatively high energy d. and low cost per kW-hour. Addnl., unlike many other types of primary battery, alk. cells can theor. be recharged. Their low cost per kW-hour makes them potentially ideal for applications such as sustainable energy storage or peak demand shaving. However, a phase transformation that occurs in MnO₂ after redn. by more than one electron converts it into the electrochem. inactive Mn₃O₄ phase. This limits the total depth of discharge of the cell significantly. We report the synthesis of a novel electrode material, manganese-doped witherite, for rechargeable alk. batteries produced by a simple hydrothermal process. The material has been studied via X-ray diffraction and electroanal. techniques. We show that unaltered witherite has poor electrochem. properties, and that this new material has high capacity and rate capability, even under deep discharge conditions, superior to conventional manganese dioxide.

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Binder, L.; Jantscher, W.; Hofer, F.; Kothleitner, G. Production and Characterisation of Electrolytically Doped Manganese Dioxide J. Power Sources 1998, 70 (1) 1– 7, DOI: 10.1016/S0378-7753(97)02564-0

[CrossRef], [CAS]

18.

Production and characterization of electrolytically doped manganese dioxide

Binder, L.; Jantscher, W.; Hofer, F.; Kothleitner, G.

Journal of Power Sources (1998), 70 (1), 1-7 CODEN: JPSODZ; ISSN:0378-7753. (Elsevier Science S.A.)

A lab. batch process for the prodn. of titanium-doped electrolytic manganese dioxide is

described. The product is characterized by chem. anal., electrochem. behavior, x-ray diffraction, and electron microscopy (TEM, ESI), including local electron energy loss spectroscopy (EELS) anal. Suggestions for possible improvement of the doping process and for the prepn. of the product are given.

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Nartey, V. K.; Binder, L.; Huber, A. Production and Characterisation of Titanium Doped Electrolytic Manganese Dioxide for Use in Rechargeable Alkaline Zinc/manganese Dioxide Batteries J. Power Sources 2000, 87 (1-2) 205– 211, DOI: 10.1016/S0378-7753(99)00487-5

[CrossRef], [CAS]

19.

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

Nartey, V. K.; Binder, L.; Huber, A.

Journal of Power Sources (2000), 87 (1-2), 205-211 CODEN: JPSODZ; ISSN:0378-7753. (Elsevier Science S.A.)

A preliminary screening test of some organo-titanium compds. was conducted. The aim was to find their chem. stability in the electrolyte used for manganese dioxide prodn. Titanium doped electrolytic manganese dioxide (Ti-EMD) samples were prepd. using suitable organo-titanium compds. and a special fine-grained titanium dioxide. The Ti-EMD samples were characterized by conducting phys., chem. and electrochem. tests on them. Phys. tests included: X-ray diffraction anal. and BET surface area detn. Chem. test conducted was the detn. of titanium content of samples. The electrochem. characterization involved: cyclic voltammetry, galvanostatic discharge and application of sample in real cell situations. Doped samples performed well in comparison with TOSOH-Hellas GH-S (com. battery grade electrolytic manganese dioxide).

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Im, D.; Manthiram, A.; Coffey, B. Manganese(III) Chemistry in KOH Solutions in the Presence of Bi- or Ba-Containing Compounds and Its Implications on the Rechargeability of γ -MnO₂ in Alkaline Cells J. Electrochem. Soc. 2003, 150 (12) A1651– A1659, DOI: 10.1149/1.1622960

[CrossRef], [CAS]

20.

Manganese(III) Chemistry in KOH Solutions in the Presence of Bi- or Ba-Containing Compounds and its Implications on the Rechargeability of γ -MnO₂ in Alkaline Cells

Im, D.; Manthiram, A.; Coffey, B.

Journal of the Electrochemical Society (2003), 150 (12), A1651-A1659 CODEN: JESOAN; ISSN:0013-4651. (Electrochemical Society)

The influence of Bi- or Ba-contg. compds. on the recharge-ability of γ -MnO₂ in alk. electrolytes was studied with AA cells contg. cylindrical cathodes and flooded cells contg. thin-film type cathodes. In addn. to the electrochem. evaluation of the cells, the discharged cathodes were analyzed by x-ray diffraction after washing and drying. The incorporation of bismuth or barium into the cathodes was found to improve the cell cyclability, which is partly due to the suppression of electrochem. inactive phases such as birnessite (δ -MnO₂) and hausmannite (Mn₃O₄). Chem. oxidn. reactions of Mn(OH)₂ with H₂O₂ in KOH medium and non-redox reactions of Mn(III) acetate with KOH followed by an anal. of the solid and filtrate indicate that the Mn³⁺ ions, which were in equil. with the solid phases contg. Mn(III), disproportionated into Mn(II) compds. and Mn(IV) oxides. Reaction mechanisms involving Mn(III) compds. in KOH soln. and the role of bismuth or barium on those reactions are discussed.

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Li, X.; Li, Z.; Xia, T.; Dong, H.; Song, Y.; Wang, L. Rechargeability Improvement of δ -Type Chemical Manganese Dioxide with the Co-Doping of Bi and Ni in Alkaline Electrolyte J. Phys. Chem. Solids 2012, 73 (10) 1229– 1234, DOI: 10.1016/j.jpcs.2012.05.018

[CrossRef], [CAS]

21.

Rechargeability improvement of δ -type chemical manganese dioxide with the co-doping of Bi and Ni in alkaline electrolyte

Li, Xiaofeng; Li, Zheng; Xia, Tongchi; Dong, Huichao; Song, Yanhua; Wang, Lizhen

Journal of Physics and Chemistry of Solids (2012), 73 (10), 1229-1234 CODEN: JPCSAW; ISSN:0022-3697. (Elsevier Ltd.)

δ -MnO₂ with the doping of Ni and Bi was prepd. through a simple chem. pptn./oxidn. method. Its structure was confirmed by the x-ray diffraction tests. The results of cyclic voltammetry and galvanostatic charge-discharge tests showed that both the doping of Bi and Ni benefited the electrochem. activity of the MnO₂ electrode. Compared to the un-doped electrode, the Bi-doped one showed larger discharge capacity and the Ni-doped one showed higher discharge potential and better cycleability. With the co-doping of 5% Bi and 10% Ni, the discharge capacity of the MnO₂ electrode reached 252 mA h g⁻¹ at a 0.2 C rate and 116 mA h g⁻¹ at a 1C rate, resp. Its capacity remained in 105 mA h g⁻¹ after 50 cycles at a 1C rate, but the capacity of a com. electrolytic MnO₂ electrode was only 37 mA h g⁻¹.

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Minakshi, M.; Singh, P.; Carter, M.; Prince, K. The Zn – MnO₂ Battery: The Influence of Aqueous LiOH and KOH Electrolytes on the Intercalation Mechanism *Electrochem. Solid-State Lett.* 2008, 11 (8) A145– A149, DOI: 10.1149/1.2932056

[CrossRef], [CAS]

22.

The Zn-MnO₂ Battery: The Influence of Aqueous LiOH and KOH Electrolytes on the Intercalation Mechanism

Minakshi, Manickam; Singh, Pritam; Carter, Melody; Prince, Kathryn

Electrochemical and Solid-State Letters (2008), 11 (8), A145-A149 CODEN: ESLEF6; ISSN:1099-0062. (Electrochemical Society)

Intercalation chem. of the zinc-manganese dioxide (Zn-MnO₂) electrochem. cell aiming at the development of aq. rechargeable batteries is presented. This study includes electrochem. characterization of MnO₂ in satd. aq. lithium hydroxide (LiOH) and potassium hydroxide (KOH) electrolytes. The lithium insertion into MnO₂ results in the formation of Li_xMnO₂. The reversible deintercalation process prevails in the presence of LiOH electrolyte. Rather than the usual protonation (H⁺) which is apparent in the literature while using KOH electrolyte, in this work, K⁺ ion insertion into MnO₂ is obsd. However, the K⁺ ion insertion is found to be irreversible. The intercalation mechanism is confirmed using various techniques to characterize the discharged MnO₂ cathode in LiOH and KOH electrolytes. The influence of small amts. of Bi₂O₃ (bismuth oxide) additive on the discharge behavior of MnO₂ is also discussed.

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23.

Minakshi, M.; Singh, P. Synergistic Effect of Additives on Electrochemical Properties of MnO₂ Cathode in Aqueous Rechargeable Batteries *J. Solid State Electrochem.* 2012, 16 (4) 1487–1492, DOI: 10.1007/s10008-011-1547-9

[CrossRef], [CAS]

23.

Synergistic effect of additives on electrochemical properties of MnO₂ cathode in aqueous rechargeable batteries

Minakshi, Manickam; Singh, Pritam

Journal of Solid State Electrochemistry (2012), 16 (4), 1487-1492 CODEN: JSSEFS; ISSN:1432-8488. (Springer)

The synergistic effect of bismuth oxide (Bi_2O_3) + titanium disulfide (TiS_2) additives in different proportions into the MnO_2 cathode material is phys. modified and tested in a Zn- MnO_2 battery with aq. LiOH electrolyte. It is found that these foreign cations stabilized the MnO_2 structure upon multiple cycling and the synergistic effect between two additives enhanced the rechargeability. This class of additive modified MnO_2 may be of interest for high-energy d. and safer batteries for applications such as elec. vehicles. The cyclability of the material suitable for elec. vehicle (EV) applications is established in this report. The incorporation of Bi_2O_3 (3 wt.%) and TiS_2 (2 wt.%) additives into the MnO_2 cathode was found to improve the cell performance, this is partly due to the suppression of proton insertion. The results on cyclic voltammetric and charge-discharge studies describing the redox mechanisms in LiOH electrolyte and the role of additives on those redox reactions are discussed and compared with that of traditional KOH electrolyte.

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Minakshi, M.Improved Performance of Bi_2O_3 -Doped MnO_2 Cathode on Rechargeability in LiOH Aqueous Cell J. Solid State Electrochem. 2009, 13 (8) 1209– 1214, DOI: 10.1007/s10008-008-0648-6

[CrossRef], [CAS]

24.

Improved performance of Bi_2O_3 -doped MnO_2 cathode on rechargeability in LiOH aqueous cell

Minakshi, Manickam

Journal of Solid State Electrochemistry (2009), 13 (8), 1209-1214 CODEN: JSSEFS; ISSN:1432-8488. (Springer GmbH)

Many attempts have been made to make the zinc-manganese dioxide (Zn-MnO_2) alk. cell rechargeable, but all investigations are pertained to the proton insertion mechanism into MnO_2 . In this paper, a new class of rechargeable bismuth oxide-doped MnO_2 electrode in lithium hydroxide (LiOH) electrolyte is described. The doping and the appropriate pH selection of the aq. electrolyte improved the electrochem. performance of the aq. cell. Hence, with an aim to understand the role of bismuth oxide (Bi_2O_3) during the discharge process, doped MnO_2 cathodes are characterized by various techniques like secondary ion mass spectrometry, X-ray diffraction, Fourier transform infra-red spectroscopy, and transmission electron microscopy anal. The results suggest that the influence of the large radius of the cation (Bi_2O_3 ; Bi (III) ion (0.96 Å)) cannot be integrated into the spinel structure, thereby, improving the rechargeability. The electrode reaction of doped MnO_2 in LiOH electrolyte is shown to be lithium insertion while preventing the formation of a spinel structure that leads to a major formation of manganese oxy hydroxides.

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Minakshi, M. Alkaline-Earth Oxide Modified MnO₂ Cathode: Enhanced Performance in an Aqueous Rechargeable Battery *Ind. Eng. Chem. Res.* 2011, 50 (14) 8792– 8795, DOI: 10.1021/ie2001742

[ACS Full Text , [CAS]

25.

Alkaline-Earth Oxide Modified MnO₂ Cathode: Enhanced Performance in an Aqueous Rechargeable Battery

Minakshi, Manickam

Industrial & Engineering Chemistry Research (2011), 50 (14), 8792-8795 CODEN: IECRED; ISSN:0888-5885. (American Chemical Society)

The current work is reported on employing alk.-earth oxide additives-i.e., barium oxide (BaO), calcium oxide (CaO), or magnesium oxide (MgO)-to the manganese dioxide (MnO₂) cathode in an environmentally safe aq. rechargeable battery. The influence of these additives on the electrochem. behavior of the MnO₂ cathode in a Zn-MnO₂ battery using lithium hydroxide (LiOH) as an electrolyte is studied. These additives enhanced the discharge performance of the Zn-MnO₂ battery and its rechargeability. Herein, the MnO₂ was phys. mixed with at least one of the alk.-earth oxides (such as BaO, CaO, or MgO) in different proportions of 1, 2, and 5% during the electrode prepn. The incorporation of BaO or MgO additives into MnO₂ results in significantly higher discharge capacity and longer cycle life, compared with the battery using CaO additive or additive-free MnO₂. The role of these additives in the MnO₂ cathode is found not to suppress the formation of nonrechargeable products, but rather to reduce the access of Zn ions to the MnO₂; without these additives, a ZnO·Mn₂O₃ product may form at the cathode.

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Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; Wiley, 2000.

There is no corresponding record for this reference.

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Croft, M.; Zakharchenko, I.; Zhong, Z.; Gurlak, Y.; Hastings, J.; Hu, J.; Holtz, R.; DaSilva, M.;

Tsakalakos, T. Strain Field and Scattered Intensity Profiling with Energy Dispersive X-Ray Scattering J. Appl. Phys. 2002, 92 (1) 578– 586, DOI: 10.1063/1.1483373

[CrossRef], [CAS]

27.

Strain field and scattered intensity profiling with energy dispersive x-ray scattering

Croft, M.; Zakharchenko, I.; Zhong, Z.; Gurlak, Y.; Hastings, J.; Hu, J.; Holtz, R.; DaSilva, M.; Tsakalakos, T.

Journal of Applied Physics (2002), 92 (1), 578-586 CODEN: JAPIAU; ISSN:0021-8979. (American Institute of Physics)

Two powerful synchrotron x-ray scattering techniques for residual strain depth-profiling and tomog.-like scatter-intensity profiling of materials are presented. The techniques utilize energy dispersive x-ray scattering, from a fixed microvolume, with micro-scanning of the specimen being used to profile its interior. The tomog.-like profiles exploit scattering-cross-section variations, and can be contrast enhanced by sep. monitoring scattering from different crystal structures. The strain profiling technique is shown to finely chronicle the internal strain variation over several mm of steel. Detailed strain profiling for a cantilever spring demonstrates the interplay of residual and external stresses in elastic/plastic deformation. Since surface compression, by shot peening, is a classic method to fortify against fatigue failure, the strain profile for a shot-peened, surface-toughened material is detd. and discussed in terms of a simple elastic-plastic stress/strain model. Finally the lattice strains in a WC/Co coated steel composite material are discussed.

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Rijssenbeek, J.; Gao, Y.; Zhong, Z.; Croft, M.; Jisrawi, N.; Ignatov, A.; Tsakalakos, T. In Situ X-Ray Diffraction of Prototype Sodium Metal Halide Cells: Time and Space Electrochemical Profiling J. Power Sources 2011, 196 (4) 2332– 2339, DOI: 10.1016/j.jpowsour.2010.10.023

[CrossRef], [CAS]

28.

In situ x-ray diffraction of prototype sodium metal halide cells: Time and space electrochemical profiling

Rijssenbeek, Job; Gao, Yan; Zhong, Zhong; Croft, Mark; Jisrawi, Najeh; Ignatov, Alexander; Tsakalakos, Thomas

Journal of Power Sources (2011), 196 (4), 2332-2339 CODEN: JPSODZ; ISSN:0378-7753. (Elsevier B.V.)

The feasibility of using energy dispersive x-ray diffraction to characterize full size battery cells is demonstrated by unprecedented in situ measurements of the electrochem. processes taking place

inside high-temp. sodium-metal halide (Na-MCl_2 , $\text{M} = \text{Ni}$ and/or Fe) cells during charge/discharge cycling. Diffraction data provide phase information either via line scans across the 5 cm wide cells or via fixed location scans as a function of time. The data confirm the propagation of a well-defined chem. reaction front, as a function of charge/discharge time, beginning at the ceramic separator and proceeding inward. Measurement of the temporal evolution of the phase abundances yields mechanistic understanding and reaction rates as a function of charge/discharge state. In the case where M includes Fe , the data also clearly show the appearance of an intermediate phase, Na_6FeCl_8 , during charging, thereby underscoring the power of this technique to reveal subtle mechanistic information. A no. of addnl. detailed electrochem. kinetic effects are also discussed. This study shows that in situ high energy x-ray diffraction characterization of advanced battery cells in space and time is eminently feasible on a routine basis, and has great potential to advance the understanding of "buried" chem. processes.

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Shen, Y.; Kordesch, K. The Mechanism of Capacity Fade of Rechargeable Alkaline Manganese Dioxide Zinc Cells. *J. Power Sources* 2000, 87 (1-2) 162-166, DOI: 10.1016/S0378-7753(99)00476-0

[CrossRef], [CAS]

29.

The mechanism of capacity fade of rechargeable alkaline manganese dioxide zinc cells

Shen, Y.; Kordesch, K.

Journal of Power Sources (2000), 87 (1-2), 162-166 CODEN: JPSODZ; ISSN:0378-7753. (Elsevier Science S.A.)

Recent expts. showed, that in contrast to traditional opinion, if the cathode was protected by anode limitation the capacity fade of Rechargeable Alk. Manganese Dioxide Zinc (RAM) cells was not caused by the EMD cathode, but by the gelled zinc anode. The key is the electrolyte. The cathode competition for the electrolyte and the increasing requirement of chem. formed ZnO for more electrolyte caused an electrolyte deficiency at the front face of the anode and finally caused pptn. of zincate and passivation of zinc. The crust is a mixed material of pptn. and passivation products. The low soly. ZnO is formed by decompn. of electrochem. generated zincate ions $[\text{Zn}(\text{OH})_4]^{2-}$ and also by recombination of zinc with oxygen during overcharge. The progressively thickened "crust" at the front face of the anode increases the resistance, then finally causes the cell to fade. The crusting is a redistribution of active material and electrolyte between the front and rear of the cylindrical gelled zinc anode. More electrolyte and proper charging can delay such a "crusting" phenomenon.

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Urfer, A.; Lawrance, G. A.; Swinkels, D. A. J. The Role of Particle Size in Cathode Optimization in Alkaline Primary Batteries J. Appl. Electrochem. 2001, 31 (3) 341– 347, DOI: 10.1023/A:1017512721635

[CrossRef], [CAS]

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The role of particle size in cathode optimization in alkaline primary batteries

Urfer, A.; Lawrance, G. A.; Swinkels, D. A. J.

Journal of Applied Electrochemistry (2001), 31 (3), 341-347 CODEN: JAELEBJ; ISSN:0021-891X. (Kluwer Academic Publishers)

In the search for cathode mixes which show max. discharge performance, cathode mixes with different electrolytic manganese dioxide (EMD) and graphite compns. have been investigated in a flooded test cell assembly. Variation in performance with particle size, both EMD and graphite, was obsd. In general, performance improved with higher amt. of graphite and finer particle size. Both lower open circuit potential and significantly better performance towards the lower potential range of the discharge occur with carbon black present. The influence of combinations of graphite and carbon black with high surface area has also been examd. The information gained can be used to better explain the influence of selected cathode materials in batteries.

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Nevers, D. R.; Peterson, S. W.; Robertson, L.; Chubbuck, C.; Flygare, J.; Cole, K.; Wheeler, D. R. The Effect of Carbon Additives on the Microstructure and Conductivity of Alkaline Battery Cathodes J. Electrochem. Soc. 2014, 161 (10) A1691– A1697, DOI: 10.1149/2.0771410jes

[CrossRef], [CAS]

31.

The Effect of Carbon Additives on the Microstructure and Conductivity of Alkaline Battery Cathodes

Nevers, Douglas R.; Peterson, Serena W.; Robertson, Logan; Chubbuck, Cameron; Flygare, Joshua; Cole, Kevin; Wheeler, Dean R.

Journal of the Electrochemical Society (2014), 161 (10), A1691-A1697 CODEN: JESOAN; ISSN:0013-4651. (Electrochemical Society)

This paper describes research to understand the relations between materials, microstructure, and performance for primary alk. battery cathodes composed primarily of electrolytic manganese dioxide (EMD). Specifically, the effect of various carbon additives on electronic transport within

cathodes was investigated. Of the various carbon additives investigated, TIMCAL BNB90 was the best performer and graphene nanopowder was the next best. These additives had the lowest Scott d. and highest BET surface area of the tested additives, and exhibited well-connected and elongated carbon pathways in SEM/FIB cross sections. Addnl., this work shows a decrease in electronic cond. for the porous cathode in the presence of KOH electrolyte. The two top-performing cathodes, when wet with concd. KOH had a cond. that was about 30% below that of the dry cond.

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Wroblowa, H. S.; Gupta, N. Rechargeable Manganese Oxide Electrodes: Part II. Physically Modified Materials J. Electroanal. Chem. Interfacial Electrochem. 1987, 238 (1–2) 93– 102, DOI: 10.1016/0022-0728(87)85167-7

[CrossRef], [CAS]

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Rechargeable manganese oxide electrodes. Part II. Physically modified materials

Wroblowa, H. S.; Gupta, N.

Journal of Electroanalytical Chemistry and Interfacial Electrochemistry (1987), 238 (1-2), 93-102 CODEN: JEIEBC; ISSN:0022-0728.

New rechargeable MnO₂ electrodes are prepd. from a variety of Mn oxides and ores by phys. admixt. of Bi and/or Pb oxides. As opposed to MnO₂ electrodes used com. or described in the literature, these phys. modified materials are rechargeable for several hundred cycles at reactant utilization within 60-95% of the theor. 2-electron capacity. The electrochem. behavior of the new electrodes is similar to that of previously described chem. modified materials: Bi and Pb birnessites. In analogy to chem. complexes of MnO₂, the fully rechargeable phys. modified materials cannot be prepd. by admixt. of foreign cations other than Bi³⁺ and Pb²⁺. The effects of Bi and Pb oxides on the reversibility of redox processes of the Mn oxide electrodes are discussed.

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33.

Abou-El-Sherbini, K. S.; Askar, M. H.; Schöllhorn, R. Hydrated Layered Manganese Dioxide:: III. Role of Bismuth Oxide on the Redox Behaviour of Hydrated Layered Manganese Dioxides Solid State Ionics 2001, 139 (1–2) 121– 133, DOI: 10.1016/S0167-2738(00)00810-9

[CrossRef], [CAS]

33.

Hydrated layered manganese dioxide: III. Role of bismuth oxide on the redox behaviour of hydrated layered manganese dioxides

Abou-El-Sherbini, Kh. S.; Askar, M. H.; Schollhorn, R.

Solid State Ionics (2001), 139 (1,2), 121-133 CODEN: SSIOD3; ISSN:0167-2738. (Elsevier Science B.V.)

The previous studies to the hydrated layered manganese dioxides were extended to show the role of bismuth oxide in the mechanism of redox reactions. The steps identified for the mechanism of the redox reactions probably are: (1) a short reversible 1-phase reaction of charge transfer $n \approx 0.23$ electron per formula unit; (2) a reversible two-phase reaction from the birnessite structure to a hydrotalcite-carbonate phase of an av. Mn oxidn. state of +2.6; and, finally, (3) another two-phase reaction from the hydrotalcite-like intermediate to manganese hydroxide. In recharging of the later phase, a two-phase reaction took place yielding β -MnOOH (Feitknechtite) which may be further oxidized to birnessite. The bismuth oxide was found to stabilize the intermediate phases (hydrotalcite during redn. or β -MnOOH during oxidn.) through the adsorption of the dissolved Bi(III) species on the active sites found mainly on the sides of the layered oxide. This adsorption formed a protective layer against the aggressive species which cause the transformation to the inactive 3-dimensional structure (e.g. Mn₃O₄). The protection is still effective as long as the adsorption equil. of bismuth species predominates.

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34.

Bode, M.; Cachet, C.; Bach, S.; Pereira-Ramos, J.-P.; Ginoux, J. C.; Yu, L. T. Rechargeability of MnO₂ in KOH Media Produced by Decomposition of Dissolved KMnO₄ and Bi (NO₃)₃ Mixtures I. Mn-Bi Complexes J. Electrochem. Soc. 1997, 144 (3) 792– 801, DOI: 10.1149/1.1837491

[CrossRef], [CAS]

34.

Rechargeability of MnO₂ in KOH media produced by decomposition of dissolved KMnO₄ and Bi(NO₃)₃ mixtures I. Mn-Bi complexes

Bode, M.; Cachet, C.; Bach, S.; Pereira-Ramos, J.-P.; Ginoux, J. C.; Yu, L. T.

Journal of the Electrochemical Society (1997), 144 (3), 792-801 CODEN: JESOAN; ISSN:0013-4651. (Electrochemical Society)

Bi-doped MnO₂ samples produced by the slow decompn. of KMnO₄ and Bi(NO₃)₃ mixts. at room temp. in 0.5 M nitric acid soln. have stable voltammograms in 1 M KOH soln. even for an extended sweep range from - 1.1 to 0.7 V vs. a normal hydrogen electrode. Anal. of the voltammograms shows the existence of complexes between Mn(X) (X = IV, III, and II) and

Bi(III), which implies the existence of formation reactions. These reactions take place during the first stage of the slow decompn. of KMnO_4 (only $X = \text{III}, \text{IV}$) and during the discharge or recharge when the dissolved $\text{Mn}(X)$ species are present in the intergranular electrolyte. X-ray diffraction studies show the absence of Mn_3O_4 when Bi(III) is present. This indicates that the reactions leading to the formation of Bi-Mn complexes prevent the hausmannite spinel lattice forming from dissolved $\text{Mn}(\text{II})$ and $\text{Mn}(\text{III})$.

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35.

Yu, L. T. Rechargeability of MnO_2 in KOH Media Produced by Decomposition of Dissolved KMnO_4 and $\text{Bi}(\text{NO}_3)_3$ Mixtures II. A Reaction Viewpoint on the Role of Bi J. Electrochem. Soc. 1997, 144 (3) 802–809, DOI: 10.1149/1.1837492

[CrossRef], [CAS]

35.

Rechargeability of MnO_2 in KOH media produced by decomposition of dissolved KMnO_4 and $\text{Bi}(\text{NO}_3)_3$ mixtures II. A reaction viewpoint on the role of Bi

Yu, L. T.

Journal of the Electrochemical Society (1997), 144 (3), 802-809 CODEN: JESOAN; ISSN:0013-4651. (Electrochemical Society)

The beneficial effect of the presence of Bi atoms on the rechargeability of MnO_2 can be explained through a reaction viewpoint. $\text{Bi}(\text{III})$ and $\text{Mn}(X)$ atoms ($X = \text{IV}, \text{III}, \text{or II}$) give stable complexes. Furthermore, the formation of Mn_3O_4 can be viewed as a stepwise 3D polymn., i.e., as a reaction chain composed of basic addn. reactions. In this way, we can easily understand that the presence of $\text{Bi}(\text{III})$ disturbs the polymn. progress, because these complex-formation reactions short-circuit the addn. reactions. When a Bi atom replaces a $\text{Mn}(\text{II})$ or $\text{Mn}(\text{III})$ atom, the building of spinel lattice is disturbed. As the size of $\text{Bi}(\text{III})$ ions ($0.96 \text{ \AA}$) are much larger than $\text{Mn}(\text{II})$ ($0.67 \text{ \AA}$) or $\text{Mn}(\text{III})$ ($0.73 \text{ \AA}$) ions, they cannot insert themselves into the spinel lattice. This prevents the formation of an extensive spinel lattice, which is well known to be a poor electroactive compd. The reaction viewpoint allows us to define two criteria for searching a beneficial effect on the rechargeability of MnO_2 material: (1) a strong interaction between the metal cations and Mn atoms is required, (2) the radius of the cation must be sufficiently large to prevent its insertion into the spinel lattice.

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36.

Qu, D. Y.; Conway, B. E.; Bai, L.; Zhou, Y. H.; Adams, W. A. Role of Dissolution of Mn(III) Species in Discharge and Recharge of Chemically-Modified MnO₂ Battery Cathode Materials *J. Appl. Electrochem.* 1993, 23 (7) 693–706, DOI: 10.1007/BF00243339

[CrossRef], [CAS]

36.

Role of dissolution of manganese(III) species in discharge and recharge of chemically-modified manganese dioxide battery cathode materials

Qu, D. Y.; Conway, B. E.; Bai, L.; Zhou, Z. H.; Adams, W. A.

Journal of Applied Electrochemistry (1993), 23 (7), 693-706 CODEN: JAELEBJ; ISSN:0021-891X.

Various exptl. techniques, including cyclic-voltammetry, const. current discharge and recharge, with a detecting electrode for detn. of sol. Mn(III) intermediate species, were used to study the reaction. mechanism involved in the redn. of a chem. modified form of MnO₂ that is multiply rechargeable. The results show how dissoln. of Mn(III) species plays an important role in the overall path of the redn. reaction. and also in the rechargeability of the material. Mainly an heterogeneous redn. mechanism is involved; substantial loss of capacity can arise if diffusion of the sol. Mn(III) species into the bulk electrolyte soln. is allowed to take place. In practical cells, this effect must be minimized using cells with starved electrolyte, i.e. with only a small free vol.-fraction of KOH electrolyte in the MnO₂-carbon electrode structure. Sol. Mn(III) species were detected in situ expts. by (a) a spectro-electrochem. procedure, (b) a collector electrode system at which dissolved Mn(III) was reoxidized to MnO₂, and (c) a rotating ring-disk electrode.

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37.

Julien, C.; Massot, M.; Baddour-Hadjean, R.; Franger, S.; Bach, S.; Pereira-Ramos, J. P. Raman Spectra of Birnessite Manganese Dioxides *Solid State Ionics* 2003, 159 (3–4) 345–356, DOI: 10.1016/S0167-2738(03)00035-3

[CrossRef], [CAS]

37.

Raman spectra of birnessite manganese dioxides

Julien, C.; Massot, M.; Baddour-Hadjean, R.; Franger, S.; Bach, S.; Pereira-Ramos, J. P.

Solid State Ionics (2003), 159 (3,4), 345-356 CODEN: SSIOD3; ISSN:0167-2738. (Elsevier Science B.V.)

Structural features of layered Mn dioxides of the birnessite family were studied using Raman scattering spectroscopy. This local probe is capable of analyzing directly the near-neighbor environment of O coordination around Mn and Li cations. Four types of sol-gel birnessite (SGB) are considered: Li birnessite (Li-Bir), Na birnessite (Na-Bir), sol-gel birnessite (SG-Bir), and sol-

gel Co-doped birnessite (SGCo-Bir). Thus, in a 1st approach, the authors consider the overall spectral features of birnessites such as the superposition of the spectra of local structures, while the lattice modes are discussed in the spectroscopic symmetry. Results show the specific spectroscopic fingerprints of SG-Bir single phases, the site occupancy of Co ions in the substituted SGCo-Bir compd., and vibrations due to Li ions with their O neighbors in Li-Bir, $\text{Li}_0.32\text{MnO}_2 \cdot 0.6\text{H}_2\text{O}$. A correlation between the interlayer d-spacing and the stretching mode frequencies of birnessite oxides was established.

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38.

Li, N.; Patrissi, C. J.; Che, G.; Martin, C. R. Rate Capabilities of Nanostructured LiMnO_4 Electrodes in Aqueous Electrolyte. *J. Electrochem. Soc.* 2000, 147 (6) 2044– 2049, DOI: 10.1149/1.1393483

[CrossRef], [CAS]

38.

Rate capabilities of nanostructured LiMn_2O_4 electrodes in aqueous electrolyte

Li, Naichao; Patrissi, Charles J.; Che, Guangli; Martin, Charles R.

Journal of the Electrochemical Society (2000), 147 (6), 2044-2049 CODEN: JESOAN; ISSN:0013-4651. (Electrochemical Society)

Nanostructured LiMn_2O_4 electrodes consisting of LiMn_2O_4 nanotubules that protrude from a current collector surface like the bristles of a brush were prep'd. using the template method. The rate capabilities of these nanostructured electrodes were studied at the 4 V (vs. Li/Li^+) potential plateau in aq. LiNO_3 electrolyte. Rate capability improved with decreasing wall thickness of the tubules which formed the electrode. This result is in agreement with the authors' prior studies of template-synthesized electrode materials which showed that rate capabilities improve with decreasing distance for Li^+ transport in the solid state. The rate capabilities of electrodes prep'd. from the smallest-wall-thickness tubules are extraordinary; these electrodes can be cycled at C rates ≤ 109 C. Probably the poor cycling performance obs'd. in prior studies of this electrode/electrolyte system results from unwanted oxidn. of water during the charging process. By controlling the charge rate and the dimensions of the nanotubules making up the template-synthesized cathodes, this unwanted side reaction can be eliminated and good cycle life is obs'd. The nanostructured electrodes offer a unique advantage to this particular electrode/electrolyte system.

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39.

Paik, Y.; Bowden, W.; Richards, T.; Sirotina, R.; Grey, C. P. ²H MAS NMR and SPECS Studies of γ -MnO₂ Reduction in Zinc Alkaline Primary Batteries J. Electrochem. Soc. 2004, 151 (7) A998– A1011, DOI: 10.1149/1.1757459

[CrossRef], [CAS]

39.

²H MAS NMR and SPECS studies of γ -MnO₂ reduction in zinc alkaline primary batteries

Paik, Younkee; Bowden, William; Richards, Thomas; Sirotina, Rimma; Grey, Clare P.

Journal of the Electrochemical Society (2004), 151 (7), A998-A1011 CODEN: JESOAN; ISSN:0013-4651. (Electrochemical Society)

²H magic-angle spinning (MAS) NMR spectroscopy was used, in conjunction with step potential electrochem. spectroscopy (SPES), to investigate the redn. and H-insertion mechanisms of γ -MnO₂ in primary zinc alk. batteries. Three electrolytic manganese dioxides (EMDs) were discharged in a deuterated alk. electrolyte: a com. EMD, and two synthetic EMDs, one prepd. in a static electrolyte, and the other in a deuterated static electrolyte. Five distinct discharge processes were obsd. in the SPES plots, which were assigned to redn. of MnO₂ near defects (1.45 V), redn. of ramsdellite and pyrolusite domains (1.1-1.3 V), formation of ZnMn₂O₄ (1.05 V), and redn. of Mn(III) to Mn(II) (0.95 V). The ²H signal intensities increase up to ca. 50% of discharge and then decrease on further discharge due to the growth of non-proton-contg. oxides, such as Mn₂O₃, Mn₃O₄, and ZnMn₂O₄. The ²H MAS NMR spectra of the 1.4 V discharged products of all γ -MnO₂ samples were dominated by an isotropic resonance at around 300 ppm, which is assigned to deuteron environments near defects (e.g., Mn-vacancy sites). The results were compared to those for three γ -MnO₂ model compds. with different levels of De Wolff disorder, Pr $\approx$ 0.25, 0.61, 0.99.

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