Manganese dioxide cathode in the presence of TiS2 as additive on an aqueous lithium secondary cell

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Abstract
Intercalation of lithium into the vacant sites of a host compound can be achieved electrochemically using nonaqueous electrolytes. The use of aqueous electrolyte is less common because of the reactivity of many lithium intercalation compounds with water. Here, we propose that lithium could be intercalated into the manganese dioxide cathode in a battery using saturated lithium hydroxide as the electrolyte. The positive electrode reaction at MnO2 in this medium is shown to be lithium insertion rather than the usual protonation, and acceptable rechargeability is observed. Using X-ray photoelectron spectroscopy and scanning electron microscope analysis on the discharged cathode material we confirmed the presence of lithium ions in the host structure of MnO2. Further, the incorporation of small amounts (<3 wt%=weight percent) of titanium disulphide (TiS2) additive to the cell MnO2 cathode leads to a significant improvement in cell performance.

Keywords
cathode, cell, secondary, lithium, aqueous, dioxide, additive, manganese, tis2, presence

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The demand for rechargeable batteries for a variety of applications, particularly in electronic devices, is constantly growing. An important aspect is the environmental threat posed by the heavy metals used in many of today’s batteries proposed or in current use. Lithium batteries also pose environmental problems. In this regard, the lithium-ion battery “rocking chair” system is an obvious choice. This battery now represents the state-of-the-art in small-size rechargeable cells for consumer electronic devices. The cathode material in this battery relies on the application of one of the well-known lithium insertion compounds LiCoO2, LiNiO2, LiMn2O4, or γ-MnO2. Insertion compounds are the ones in which the rigid host lattice of the compound remains unchanged after repeated insertion and extraction of lithium or any other foreign atoms. Recently, materials based on transition metal polyanions have also been proposed, and phosphate compounds crystallizing as Nasicon structures appear to hold particular promise as a potential cathode material. For instance, it has been suggested that olivine-type lithium iron phosphate, LiFePO4, may offer the optimal combination material. The use of aqueous electrolyte is less common because of the reactivity of many lithium intercalation compounds with water. Intercalation of lithium into the vacant sites of a host compound can be achieved electrochemically using nonaqueous electrolytes.

The overall reaction of the alkaline Zn/MnO2 battery using LiOH electrolyte is less common because of the reactivity of many lithium intercalation compounds with water. For instance, it has been suggested that olivine-type MnO2 is not suitable for its reversibility, because during discharge incorporation of lithium ions into the MnO2 structure during the discharge process. Hence, in one of our previous studies we confirmed the presence of lithium ions in the host structure of MnO2. Further, the incorporation of small amounts (<3 wt % = weight percent) of titanium disulphide (TiS2) additive to the cell MnO2 cathode leads to a significant improvement in cell performance.

The main objectives of this paper are to report on

1. Understanding the discharge mechanism in aqueous lithium hydroxide electrolyte via surface characterization using various physical techniques.
2. Improvement in cell performance by adding small amounts (<3 wt %) of titanium disulphide (TiS2) to the cathode and its rechargeability.

**Experimental**

The γ-MnO2 of battery grade material used in this work was purchased from Sigma Aldrich. Titanium disulphide (TiS2) was obtained from Alfa Aesar. For the electrochemical test, a pellet was prepared by mixing 70–75 wt % MnO2 consisting of 0–5 wt % TiS2, 20 wt % acetylene black (A-99, Asbury, USA) and 5 wt % poly (vinylidene difluoride) (PVDF, Sigma Aldrich) binder in a mortar and pestle. A Swagelok-type electrochemical cell was constructed with the disklike pellet as the cathode, Zn metal as the anode, and filter paper (Whatman filters 12) as the separator. The electrolyte was a saturated solution of lithium hydroxide (LiOH) containing 1 mol L−1 zinc sulphate (ZnSO4). The cells were discharged-charged galvanostatically at 0.3 mA/cm2 by using an EG&G Princeton Applied Research potentiostat/galvanostat model 273 A, operated by model 270 software (EG&G). The cutoff discharge and charge voltages were 1.0 and 1.8 V, respectively. Reported potentials are relative to Zn metal. All electrochemical measurements were carried out at ambient atmosphere. The products formed during charge and discharge cycles were characterized by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) techniques. XPS (Kratos Ultra Axis spectrometer) using monochromatic Al Kα (1486.6 eV) radiation was used to analyze the chemical binding energy of the samples. XPS analysis was started when the pressure in the analysis chamber fell below 1 × 10−9 hPa. Carbon, C (1s), was used as a reference for all the samples. The surface analysis of the materials was conducted by using a scanning electron microscope (Philips Analytical XL series 20).

**Results and Discussion**

Electrochemical behavior of MnO2 in aqueous LiOH cell.— Figure 1 shows the discharge-charge characteristics of the
the Mn4+/3+ redox couple, the practically realizable capacity of the voltage suddenly fell to 1.0 V. The 1.6 V region could correspond to an ally decreased to 1.4 V. The discharge was terminated when the open-circuit voltage dropped rapidly during the first 20 cycles from 82 to 56%, after the tenth cycles, respectively. After a few cycles the loss in capacity stabilized and the cell was able to deliver as many as 40 cycles with a discharge capacity of 70 mAh/g. The coulombic efficiency of the material is found to be 140 mAh/g. The percentage of material utilization was 50%. During the charge process, from 1.3 V there was a constant increase in potential up to the charge cutoff voltage of 1.8 V. As can be seen in Fig. 1, the cell could be reversibly discharged and charged.

The rechargeability of the cell Zn-MnO2 was investigated and the results are shown in Fig. 2. The MnO2 cathode could deliver a reversible capacity of about 138 and 110 mAh/g for the second and tenth cycles, respectively. After a few cycles the loss in capacity stabilized and the cell was able to deliver as many as 40 cycles with a discharge capacity of 70 mAh/g. The coulombic efficiency dropped rapidly during the first 20 cycles from 82 to 56%, after which the decrease was gradual. At the 40th cycle the efficiency was decreased to 45%. This behavior indicates that the material is rechargeable in aqueous solutions.

In order to evaluate the effect of discharge current on the MnO2 cathode in aqueous LiOH electrolyte, we performed the discharge process with various discharge currents between 0.1 and 1.0 mA, and their results are shown in Fig. 3. The observed discharge capacity at relatively low currents of 0.1, 0.3, and 0.5 mA is 150, 140, and 105 mAh/g. An increase in the current to 0.7 and 1.0 mA results in an important decrease of the discharge capacity from 150 to 55 and 25 mAh/g, respectively. In the discharge curve for higher current (0.5 mA) the Mn4+/3+ redox couple region was slightly shifted to a lower voltage. For the discharge current of 1.0 mA the Mn4+/3+ redox couple region has not been well observed within the cutoff voltage. This abrupt drop in voltage signals that a reduction of manganese is not complete. The capacity loss occurring at a high rate of discharge (0.7 and 1.0 mA) in Fig. 3 is not irreversible. The capacity is regained on returning to low discharge current of 0.1 and 0.2 mA, which shows that the loss of capacity is likely to be a kinetic effect. Hence, the cell is able to sustain the discharge current limit of 0.5 mA.

**Figure 2.** Discharge curves for various cycles illustrating the cyclability of MnO2 samples.

**Figure 3.** Effect of various discharge currents on the first discharge cycle for the Zn-MnO2-aqueous battery.

Zn-MnO2-aqueous lithium hydroxide cell. The cell was discharged and charged galvanostatically (0.3 mA/cm²) to 1.0 and 1.8 V, respectively. On commencement of discharge, the voltage dropped from the open-circuit voltage (OCV) 1.85 to 1.7 V and then gradually decreased to 1.4 V. The discharge was terminated when the voltage suddenly fell to 1.0 V. The 1.6 V region could correspond to the Mn4+/3+ redox couple. The practically realizable capacity of the voltage dropped rapidly during the first 20 cycles from 82 to 56%, after which the decrease was gradual. At the 40th cycle the efficiency was decreased to 45%. This behavior indicates that the material is rechargeable in aqueous solutions.

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**Physical characterization of the discharged cathode material.**—The cathode material formed during the discharge cycle was characterized by using physical techniques, i.e., SEM and XPS.

The morphology of the MnO2 before and after discharge and recharged samples has been studied via SEM. Examination of the surface of MnO2 uncycled cathode via SEM (Fig. 4a) revealed that the particle size is of the order of 20–25 μm. On discharge, Fig. 4b, the micrograph shows the absence of this agglomeration. However, the structural irreversibility of the starting MnO2 is observed in the morphology, and is most likely the reason for the loss in cell capacity after various cycles, as shown in cycling behavior, Fig. 2.

Due to the low crystallinity of the starting material, the X-ray diffraction (XRD) pattern showed only broad Bragg reflections. The discharged cathode was covered with a thick layer of materials after various cycles, as shown in cycling behavior, Fig. 2.
thick layer of materials (like LiOH, Li₂CO₃, and H₂O) on the surface of the discharged products. The lithium carbonate is the result of LiOH electrolyte reacting with atmospheric carbon dioxide. Figure 5 and 6 show the XPS spectra of C (1s) and Li (1s) region of the discharged cathode MnO₂. As can be seen in Fig. 5, the Li₂CO₃ peak had a very strong signal before argon ion bombardment and then decreased in intensity on continuous etching of the surface layer, indicating that the Li₂CO₃ layer was removed. The hydrocarbon peak at 285 eV had a strong intensity before argon ion bombardment, whereas after 40 min and 1 h etching it decreased in intensity towards a lower binding energy of 284 eV. Figure 6 shows the XPS spectra of Li (1s) region. It can be seen in the figure that upon argon etching the peak corresponding to 55.6 eV starts to disappear. Instead, a new peak emerged at 54.7 eV. The intensity of the signal for the new peak at 54.7 eV remained fairly constant upon argon ion etching. Based upon binding energies as reported,¹⁴,¹⁵ we assign the peak at 55.3 eV to Li₂CO₃ and the second peak at 54.7 eV to intercalated lithium. The basis of this assignment is that during the reduction process lithium has been intercalated into the MnO₂ cathode from aqueous LiOH solution. Hence, the XPS profiles of Fig. 5 and 6 show that Li is present in the carbonate layer as Li₂CO₃ and in MnO₂ as intercalated lithium.

From the evidence based on the XPS depth profiles, it can be concluded that formation of Li₂CO₃ occurs on the cathode MnO₂ surface, which inhibits the diffusion of OH⁻ but permits the Li⁺ ion to undergo intercalation into the active layer of the γ-MnO₂ host material as shown in Eq. 2. This would provide an intercalation mechanism for a secondary aqueous cell.

**Effect of TiS₂ additive in the MnO₂ cathode.**— The influence of TiS₂ as an addition to manganese dioxide cathode on the performance of an aqueous lithium hydroxide electrolyte battery was investigated. This was motivated by studies which have shown the beneficial effects of Bi³⁺ and other ionic additions.¹⁶-¹⁹ A potential candidate in this regard has been Ti⁴⁺ ion.¹⁵ In this work, small amounts of TiS₂ as additives have been employed by physically mixing TiS₂ powder into the cathode and investigating the effects of this on the electrochemical behavior. In order to determine if there was any influence of this additive on the MnO₂ structure, SEM and XPS have been performed. The morphology of the surface of MnO₂ in the presence of various amounts of TiS₂ as additive is shown in Fig. 7. The SEM micrograph with the additive of the 5 wt % shows a little change in morphology, i.e., rounded particles around 10 µm in diameter. Apart from this no other information relating to structural changes can be drawn from SEM. Figure 8 shows the XPS spectra of the Mn 2p region for the γ-MnO₂ cathode material with various wt % of TiS₂ additive. For 1 and 3 wt % samples, peaks are well defined and are more intense that those of the 5 wt % material, where only a shoulder of peak is seen and shifted 1 eV towards lower binding energy. This shows that increasing the additive from 3 to 5 wt % alters the manganese state in MnO₂. Its corresponding infrared spectra analysis has been performed (not included here) and agrees well with the
XPS data. This suggests that the bonding of Mn in MnO$_2$ has been slightly altered by physically mixing it$^{18}$ with TiS$_2$ at higher weight loadings.

Figure 9 shows the performance of the MnO$_2$ cell as a function of TiS$_2$ loading. For the plain MnO$_2$ (without additive) the observed capacity is 150 mAh/g (from Fig. 1). With 1 wt % additive, there was an increase in capacity value from 150 to 175 mAh/g, although it is negligible. For a cell with 3 wt % additive, electrode capacity dramatically increased to 260 mAh/g, whereas, for a cell with 5 wt % additive, capacity decreased to 75 mAh/g. Although the shape of the discharge curve remains unchanged for the various wt %, the average voltage is significantly altered for 5 wt %. The cell could be reversibly discharged and charged, and a significant voltage polarization is seen for 5 wt % additive. The increase in discharge capacity could be explained in terms of the TiS$_2$ additive stabilizing the MnO$_2$ octahedra (as seen in Fig. 8) towards dimensional changes that occur during the discharge process.$^{18}$ However, increasing the additive content from 3 to 5 wt % causes a decrease in the cell voltage and capacity. This result is in accordance with the XPS and IR spectra revealing that the Mn state in MnO$_2$ is altered by physical mixing of additives.

The discharge curves for the first ten cycles illustrating the cyclability for 3 and 5 wt % additive are shown in Fig. 10 and 11, respectively. The cycling performance is quite good in 3 wt % without much irreversible capacity as seen for 5 wt % additive in Fig. 11. However, a slight inflection around 1.5 V is seen only for MnO$_2$ containing additive. Figure 12 compares the cycling performance of

Figure 7. Scanning electron micrographs of the MnO$_2$ cathode in the presence of small amounts of TiS$_2$ additive.

Figure 8. XPS spectra of Mn 2p for the MnO$_2$ cathode with TiS$_2$ additive.

Figure 9. The first discharge-charge profiles of Zn-MnO$_2$ cells containing TiS$_2$ additive.

Figure 10. Discharge curves for various cycles illustrating the cyclability of MnO$_2$ containing 3 wt % additive.
The Zn-MnO₂ cells for the first ten cycles in the presence of 0, 3, and 5 wt % additive. The available capacity is low and decreases quickly for the 5 wt % additive. The plain MnO₂ cell shows significantly improved capacity, although this is still less than that of 3 wt % additive. The cell capacity for 3 wt % additive is high and decreased gradually for the first five cycles (from 260 to 192 mAh/g, reflecting a loss of 25%) then stabilized with a loss of only 13% at the tenth cycle. Although the plain MnO₂ shows improved capacity retention during cycling, its energy density is lower than that of 3 wt % additive.

Based upon the results discussed above, it can be concluded that at 3 wt % loading of the TiS₂ additive stabilizes the MnO₂ crystalline structure and this leads to a high cell capacity. At the highest weight loading (5 wt %) the crystalline structure is no longer stabilized by TiS₂ and the cell capacity decreases.

Conclusions

The characterization of the products formed when MnO₂ is discharged in a Zn-MnO₂ in aqueous LiOH cell indicates that the cell discharge mechanism involves Li⁺ intercalation into the host structure. This is confirmed by analysis of the products formed on the discharged MnO₂ cathode by using SEM and XPS techniques. Small amounts of TiS₂ additive into the MnO₂ cathode improve the discharge capacity by stabilizing the structure of MnO₂. However, increasing the additive content above 3 wt % causes a decrease in the cell voltage and discharge capacity.

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