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The effect of B₄C addition to MnO₂ in a cathode material for battery applications

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Abstract

Boron carbide (B₄C) added manganese dioxide (MnO₂) used as a cathode material for a Zn–MnO₂ battery using aqueous lithium hydroxide (LiOH) as the electrolyte is known to have higher discharge capacity but with a lower average discharge voltage than pure MnO₂ (additive free). The performance is reversed when using potassium hydroxide (KOH) as the electrolyte. Herein, the MnO₂ was mixed with 0, 5, 7 and 10 wt.% of boron carbide during the electrode preparation. The discharge performance of the Zn|LiOH|MnO₂ battery was improved by the addition of 5–7 wt.% boron carbide in MnO₂ cathode as compared with the pure MnO₂. However, increasing the additive to 10 wt.% causes a decrease in the discharge capacity. The performance of the Zn|KOH|MnO₂ battery was retarded by the boron carbide additive. Transmission electron microscopy (TEM), and energy dispersive X-ray spectroscopy analysis (EDS) results show evidence of crystalline MnO₂ particles during discharging in LiOH electrolyte, whereas, manganese oxide particles with different oxygen and manganese counts leading to mixture of phases is observed for KOH electrolyte which is in agreement with X-ray diffraction (XRD) data. The enhanced discharge capacity indicates that boron atoms promote lithium intercalation during the electrochemical process and improved the performance of the Zn|LiOH|MnO₂ battery. This observed improvement may be a consequence of B₄C suppressing the formation of undesirable Mn(III) phases, which in turn leads to enhanced lithium intercalation. Too much boron carbide hinders the charge carrier which inhibits the discharge capacity.

Keywords; Boron carbide; TEM; Zn–MnO₂ battery

1. Introduction

In the early 1960s, alkaline Zn/MnO₂ batteries were introduced and widely accepted for several benefits such as long service life, low internal resistance, cost-effectiveness, acceptable low temperature performance and long-shelf life at ambient temperature with respect to other alkaline batteries [1]. Recent advancements in electronic devices such as digital cameras, MP3 players and high-tech toys require alkaline batteries to function under high rate conditions. In this regard, manganese dioxide, with high purity and sufficient electrochemical activity under a range of discharge conditions, as a cathode and with Zn as an anode can be produced efficiently and inexpensively for commercial purposes [2].

Enhanced electrochemical performance of MnO₂ has opened the bottle neck to improve Zn–MnO₂ battery performance. Various studies have shown that the presence of small amounts of additives such as Bi₂O₃, PbO₂ or BaTiO₃[3], [4] and [5] significantly improves discharge performance however without greatly improving their recharge capacity. Hence Zn–MnO₂ remains as the primary battery. Recently, we showed that lithium intercalation can occur in a Zn–MnO₂ battery using aqueous LiOH electrolytes and made the primary battery as secondary [6]. In order to enhance the overall performance of this aqueous secondary battery, we have investigated various additives such as TiS₂, TiB₂, Bi₂O₃, CaO and CeO₂[7], [8], [9] and [10] which are physically added to the MnO₂ cathode during electrode preparation. These additives enhanced the lithium intercalation while suppressing the formation of non-rechargeable products like Mn₃O₄ and MnOOH [7], [8], [9] and [10].

In this paper, we report on boron carbide (B₄C) added MnO₂ cathodes that cause an increase in capacity but with a low average voltage profile. Boron-doping into graphite to improve the discharge capacity of the graphite electrode in a lithium battery using non-aqueous solvent as electrolyte [11], [12] and [13] is a well-known area of research. Boron as an electron acceptor/donor modifies strongly the electronic properties of the host compound without any large distortion of the crystal lattice

[12] and [13]. Herein, B₄C has been used in as an additive to MnO₂ cathode material for the first time. The objective of this work is to understand (a) the influence of B₄C additive to MnO₂ on overall battery performance (b) the effect of additives on the intercalation mechanism and (c) the desired amount of additives to modify battery performance and to obtain high discharge capacity.

2. Experimental

2.1. Materials and methods

The EMD (electrolytic manganese dioxide; γ -MnO₂) type (IBA sample 32) material used in this work was purchased from the Kerr McGee Chemical Corporation. B₄C was obtained from Cerac Inc. For the electrochemical test, a pellet was prepared by mixing 65–75 wt.% MnO₂ with 0–10 wt.% B₄C, 15 wt.% acetylene black (A-99, Asbury, USA) and 10 wt.% poly vinylidene difluoride (PVDF, Sigma–Aldrich) binder in a mortar and pestle. An electrochemical cell was constructed with the disk-like pellet (of 8 mm diameter and 0.5 thickness) 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) with a pH equivalent to 10.5. The mass of zinc was at least ten-fold in excess of that required for the stoichiometric reaction between Zn and MnO₂. The cell design and its experimental details were similar to those reported earlier [6] and [9]. The cells were discharged/charged galvanostatically using an EG&G Princeton Applied Research Potentiostat/Galvanostat model 273 A, operated by model 270 software (EG&G). The cut-off discharge and charge voltages were 1.0 and 1.9 V, respectively.

The morphology of the products formed before and after discharge was characterized by transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy analysis (EDS) using a JEOL 2010F TEM operated at 200 kV. TEM specimens were prepared by grinding a small fragment scraped from the pressed pellet under ethanol and dispersing on a holey carbon support film.

A Siemens D500 X-ray diffractometer 5635 using Co-K α radiation was used for X-ray diffraction analysis (XRD). The voltage and current were 30 kV and 40 mA, respectively. The scan rate was 1°/min between two theta values of 20° and 60°.

3. Results and discussions

3.1. TEM studies of the material before discharge

Bright field TEM images of the boron carbide (5 wt.%) added MnO₂ before discharge are shown in Fig. 1. Throughout this paper, the term “sp” on figures indicates the position from which EDS spectra were recorded. Fig. 1a shows the MnO₂ before discharge is composed of submicron clumps of individual crystals. Selected area electron diffraction confirmed the MnO₂ to be crystalline. B₄C particles were scarce and tended to be several microns in size with MnO₂ clumps adhering to the surface (Fig. 1b). This indicates that the boron carbide is not dissolved and then dispersed throughout the MnO₂ cathode material

3.2. Galvanostatic studies

3.2.1. Discharge characteristics in LiOH and KOH electrolyte

Fig. 2 compares the discharge characteristics of the B₄C added MnO₂ with Zn as an anode in LiOH electrolyte. The discharge capacity of the B₄C added MnO₂ to ≤ 7 wt.% is increased significantly as compared with the pure MnO₂, i.e. from 145 to 230 mAh/g. However, increasing the additive of B₄C to 10 wt.% causes a decrease in its discharge capacity to 110 mAh/g. Although 7 wt.% of B₄C enhanced the discharge capacity, a rapid capacity fade on long term cycling was measured [14]. It is also found that the cell voltage for all B₄C added MnO₂ cathodes are lower than pure MnO₂ (0 wt.% additive). The mid discharge voltage decreases by 0.1 V with the amount of additives. The behavior of these cells as a function of boron concentration could be explained qualitatively if the boron is

considered as an electron donor [15]. Boron has three valence electrons, one electron more than manganese, therefore when added into a MnO_2 host lattice, acts as an electron donor. However, during the discharge process, when lithium is inserted into the manganese host the additive boron carbide acts as an electron acceptor, accepting its 2 s electron to the manganese host. This charge transfer is an effect that suggests the presence of boron weakens the chemical bond between the lithium intercalated MnO_2 (Li_xMnO_2) and the B_4C added MnO_2 compared to the pure MnO_2 . The strength of the bond determines the chemical potential of the MnO_2 which in turn determines the cell voltage. As a result, the potential of the B_4C added MnO_2 could be decreased relative to the additive free cell (in Fig. 2). This is further evidenced in the case of KOH electrolyte (in Fig. 3). The presence of boron carbide weakens the potassium host bond compared with a pure MnO_2 that lowers the average cell by 0.2 V. The performance of the KOH battery was retarded with the addition of boron carbide.

Fig. 3 compares the discharge characteristics of the B_4C added MnO_2 with Zn as an anode in KOH electrolyte. The discharge capacity of the pure MnO_2 (0 wt.% added) is found to be 240 mAh/g, which is 60% higher than that obtained for LiOH electrolyte (seen in Fig. 2). However, the discharge capacity of the B_4C added MnO_2 (5, 7 and 10 wt.%) decreased significantly to 200, 165 and 75 mAh/g respectively. The discharge behavior of this battery is very different from the LiOH battery. The difference can be explained in terms of Li^+ and K^+ ion insertion [16]. The KOH cell involves K^+ ion insertion from the electrolyte into the MnO_2 cathode which inhibits the usual H^+ mechanism for further rechargeability. Hence, this cell was deteriorated with the discharge capacity.

The increase in discharge capacity with the addition of boron carbide to ≤ 7 wt.% in LiOH battery (Fig. 2) is probably due to boron carbide incorporation into the MnO_2 structure. Since boron is known to be a fast diffusant, it should have found an interlayer site in the MnO_6 octahedra. This interlayer site undergoes an expansion with boron additive and aids in promoting the lithium intercalation from

the LiOH solution during discharge process. This causes an increase in capacity, however too much boron carbide will interrupt the entrance of the charge carriers to MnO₂ sites which results in a decrease in capacity. Hence, addition of 7 wt.% B₄C was shown to be the optimal amount to modify the battery performance in MnO₂ cathode. In the case of KOH electrolyte (Fig. 3), no improvement of battery performance was found. This may be because proton/K⁺ ion insertion is not viable with the boron carbide additive. Additionally, the inserted K⁺ ion is not reversible hence the battery remains primary. In order to increase the discharge capability in the Zn/MnO₂ cell using either LiOH or KOH electrolyte, anodes made from as-prepared zinc powder with high surface area could greatly reduce the Zn(OH)₂ passivation leading to anodic failure.

3.3. Physical characterization of the discharged cathode

3.3.1. TEM and EDS analysis

In order to elucidate the role of boron carbide in the LiOH and KOH electrolyte, the discharged MnO₂ was characterized using TEM, EDS and XRD techniques. Bright field TEM images of the B₄C (5 wt.%) added MnO₂ cathodes after the first discharge cycle in LiOH electrolyte are shown in Fig. 4. The general morphology of the MnO₂ clumps is similar to the original material but individual crystals appear to be less distinct. The magnified image (Fig. 4b) and corresponding EDS spectra (Fig. 4c) shows crystalline particles of MnO₂ (Sp₄) and regions of polycrystalline zinc oxide (Sp₃) deposited from the electrolyte. EDS spectra recorded from the MnO₂ regions invariably contained small amounts of Zn which is from the electrolyte. Based on this, it is proposed that reduction of Mn occurs via intercalation of lithium forming crystalline particles of MnO₂. The presence of boron carbide appears to have increased the intercalation process.

Bright field imaging of the B₄C (5 wt.%) added MnO₂ cathode discharged in KOH electrolyte (Fig. 5a and b) showed a similar morphology to that seen for LiOH electrolyte. Once again, crystalline

MnO₂ clumps and polycrystalline Zn oxide regions were observed (Fig. 5c). The MnO₂ clumps contained both Zn and K. Zn oxide regions also contained K. Fig. 6 shows EDS spectra from selected areas of Fig. 5c. The electrode reaction of MnO₂ in KOH electrolyte is protonation leading to various Mn oxides and hydroxides such as Mn₃O₄ and MnOOH with evidence of potassium ion insertion seen in EDS spectra. However, given the type of the specimen used here, it is hard to distinguish whether the K⁺ ions are from the surface layer or intercalated species.

3.3.2. XRD analysis

The intercalation mechanism is further evidenced by X-ray diffraction analysis on the material before and after the discharge process. Fig. 7a–c shows X-ray diffraction patterns of the B₄C (5 wt.%) added MnO₂ cathode before and after discharge in LiOH and KOH electrolyte, respectively. The material before discharge (Fig. 7a) shows the characteristic peaks of MnO₂ (+) and boron carbide (B) as quoted in the JCPDS cards [17] and [18]. The cathode discharged in LiOH electrolyte (Fig. 7b) shows the emergence of new peaks (●, □). The main Bragg reflection peak corresponding to graphite (acetylene black) is seen at $2\theta = 30^\circ$ (C). The original peaks MnO₂ (+) are replaced by those of a new phase corresponding to a lithium intercalated MnO₂ (Li_xMnO₂) (●) with a minor phase formation of Mn₂O₃ (□). The XRD pattern for a cathode discharged in KOH electrolyte (Fig. 7c) shows new reflections corresponding to Mn₃O₄ (○). These products are consistent with electron reduction of MnO₂ in KOH electrolyte [19]. This involves the insertion of protons/K⁺ from the electrolyte into the MnO₂ structure and the reduction reaction results in a formation of Mn₃O₄. The addition of boron carbide enhances the discharge capacity while promoting the lithium insertion in LiOH battery but retards the performance of the KOH battery due to insertion of protons/K⁺.

3.4. Multiple discharge–charge cycling

To investigate the rechargeability, 5 wt.% B₄C added cell was tested for multiple cycles and their results are compared in Fig. 8. The cell is able to discharge and charge reversibly. The discharge and charge capacity of about 175 and 165 mAh/g was achieved for the first two cycles. After further cycling, the efficiency of the cell dropped to 110 mAh/g after 25 cycles, corresponding to a 38% loss in capacity. Although the material is rechargeable the fade in capacity is significant on cycling for this B₄C added MnO₂ cell in comparison to that of our earlier studies on Bi₂O₃ and CeO₂ added cell [9] and [10].

4. Conclusions

When aqueous LiOH was used as the electrolyte B₄C added manganese dioxide (MnO₂) exhibited enhanced discharge capacity, while lowering the average discharge cell voltage. However, both the capacity and the voltage were reduced in KOH electrolyte. The difference was explained in terms of intercalation mechanism. The reason for the good electrochemical performance in LiOH electrolyte is that the presence of ≤ 7 wt.% boron broadens the pathway between the structural chains of MnO₆ octahedra for the diffusion of lithium in the host MnO₂ and stabilizes the structure. Addition of 7 wt.% is a suitable content for MnO₂ electrodes. The addition of boron carbide causes a decrease in the capacity in the cell containing KOH electrolyte this seems to indicate that proton/K⁺ ion insertion is not viable, hence the electrochemical behavior is not reversible. This is based on considering the small radius of Li⁺, whereas the case is different with potassium hydroxide electrolyte.

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Fig. 1.

TEM images of the B_4C (5 wt.%) added MnO_2 before discharge showing (a) bright field image of MnO_2 clumps and (b) large particle of B_4C (sp3) with small MnO_2 clumps attached (sp4–6). Term “sp” refers EDS spectra.

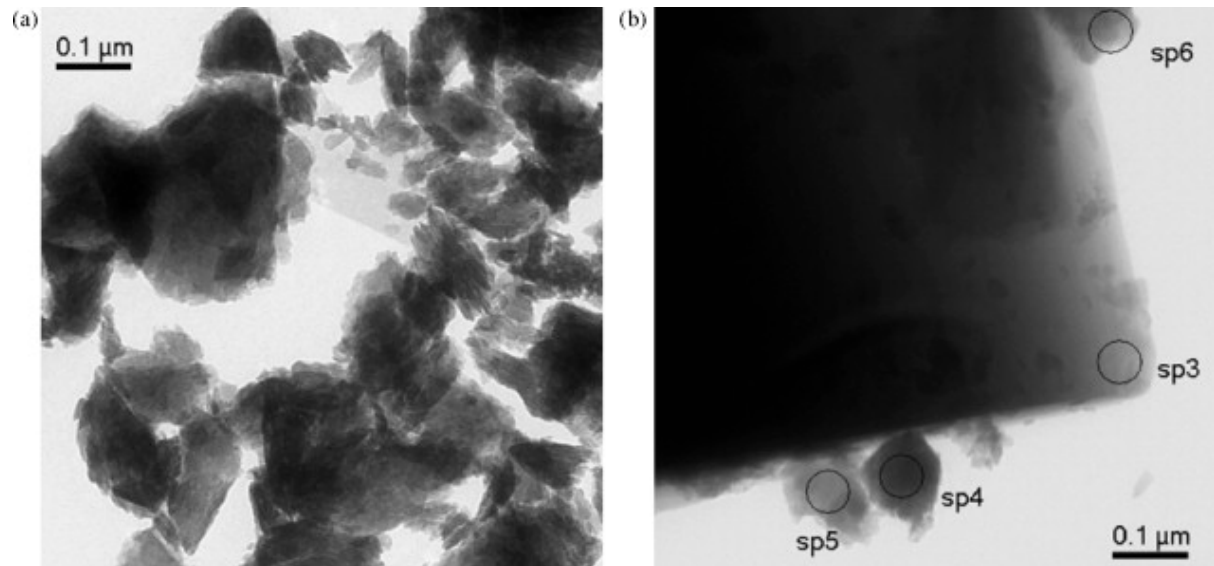


Fig. 2.

Comparison of the first discharge profile of B₄C added MnO₂ cathode (weight percent indicated in the profiles) using saturated aqueous LiOH containing 1 mol l⁻¹ of ZnSO₄ as the electrolyte.

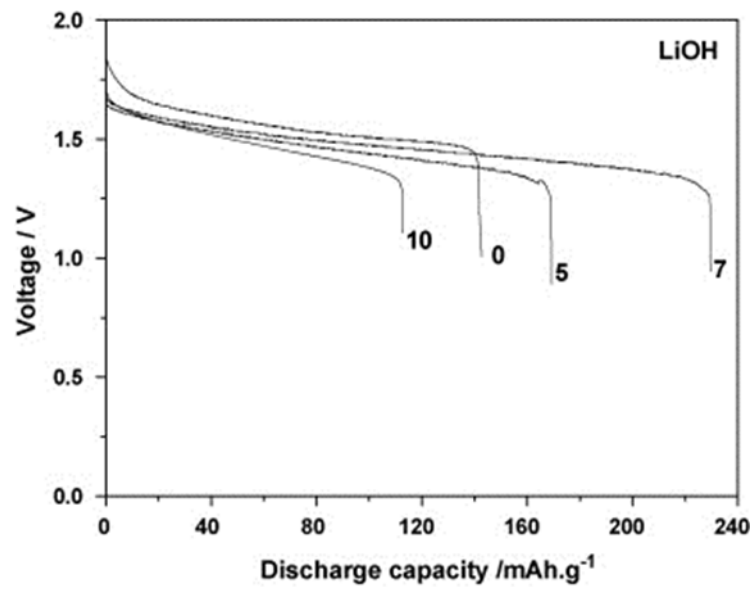


Fig. 3.

Comparison of the first discharge profile of B4C added MnO₂ cathode (weight percent indicated in the profiles) using saturated KOH as the electrolyte.

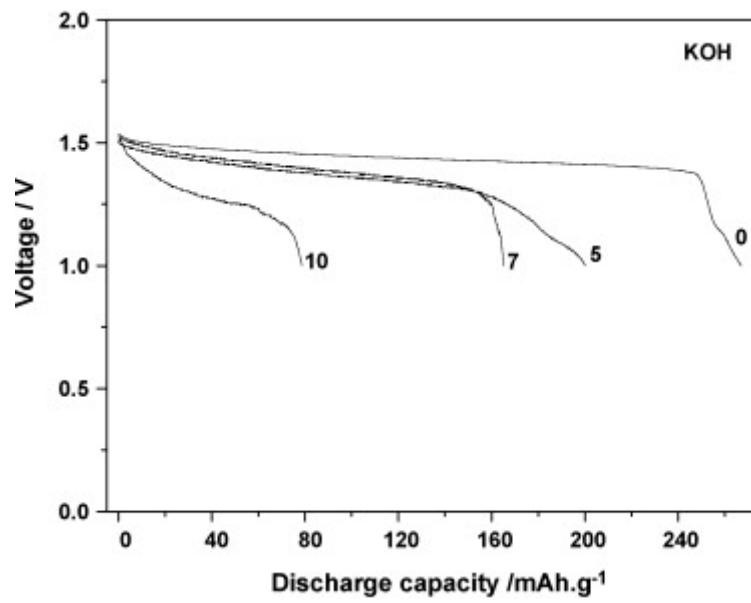


Fig. 4.

TEM image of the B_4C (5 wt.%) added MnO_2 discharged in $LiOH$ solution (a) bright field image of clustered MnO_2 and its magnified image (b) showing crystalline particles of Zn oxide (sp3) and Mn oxide (sp4) and (c) its corresponding EDS spectra of locations sp3 and sp4. Elements are shown in the figure.

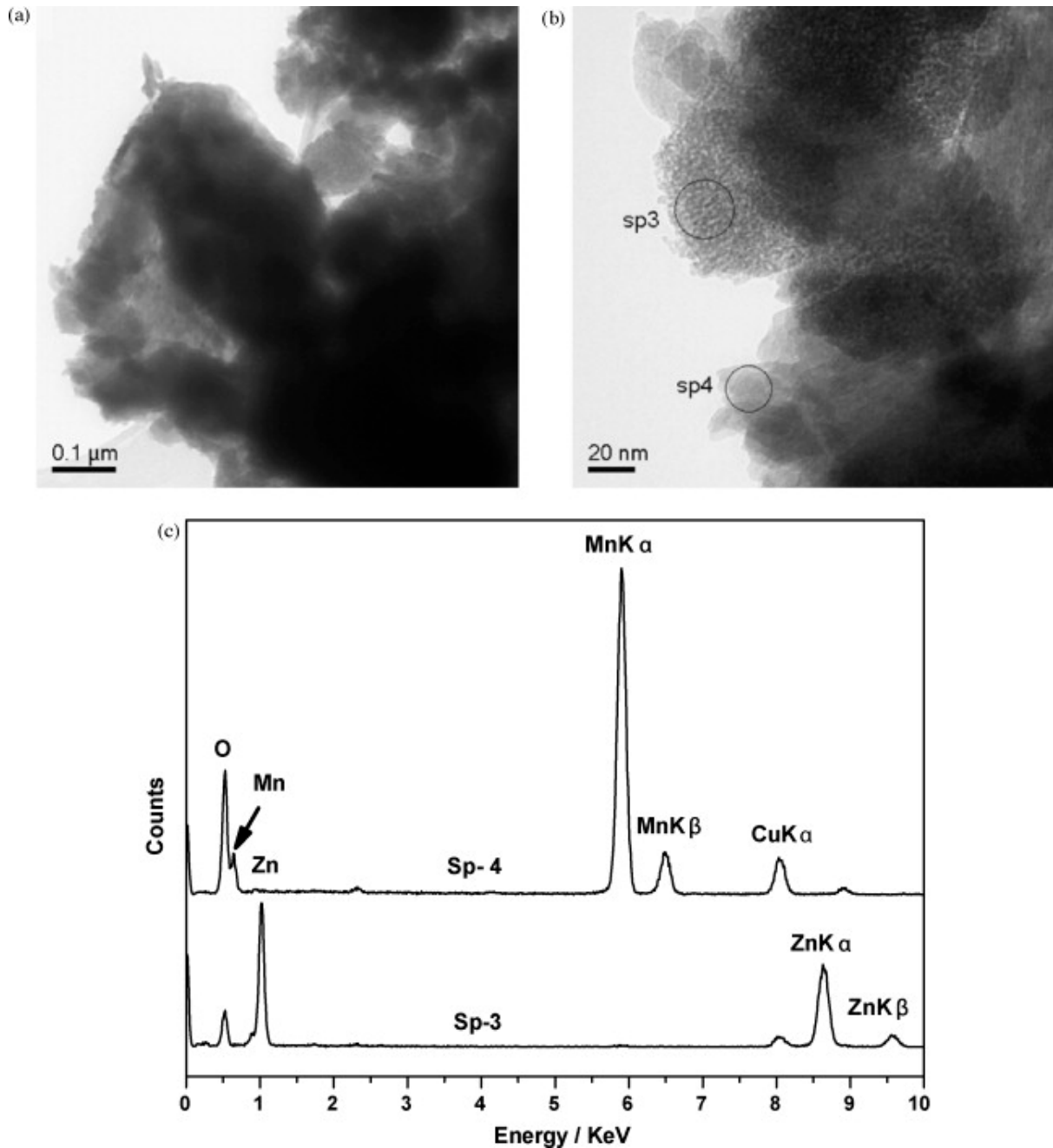


Fig. 5.

TEM images of the B₄C (5 wt.%) added MnO₂ discharged in KOH solution (a) region rich in MnO₂ showing particles are clustered, (b) magnified image showing the fine scale structure of MnO₂ (sp1–2) and a region of Zn oxide (sp3), (c) regions of mixed MnO₂ and Zn oxide (sp11–15) associated with sheets of graphite.

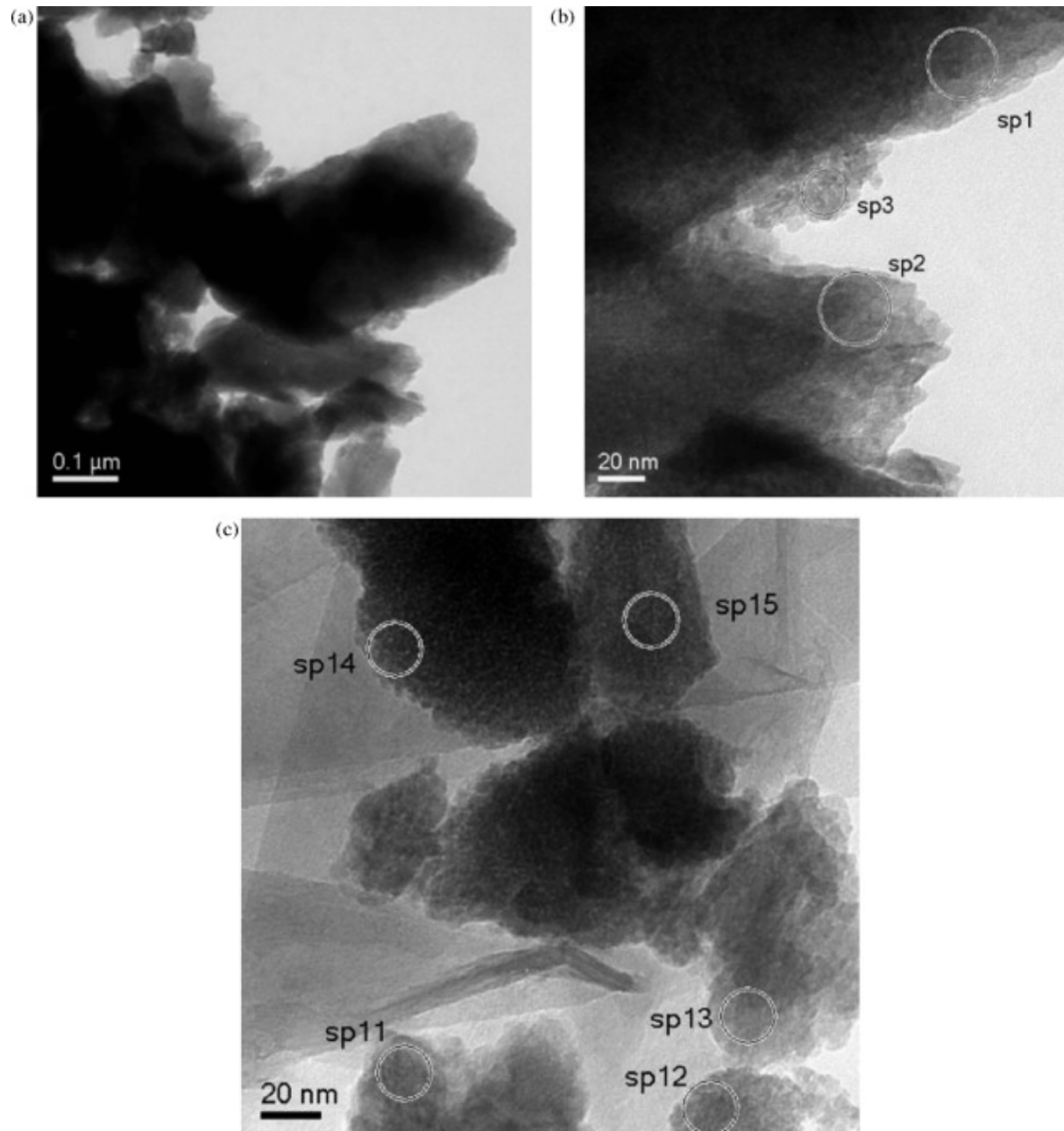


Fig. 6.

EDS spectra of the B_4C (5 wt.%) added MnO_2 discharged in KOH electrolyte. Spectra (Sp11–13) show a different oxygen and manganese contents corresponding to the TEM images in Fig. 5c. Elements are shown in the figure.

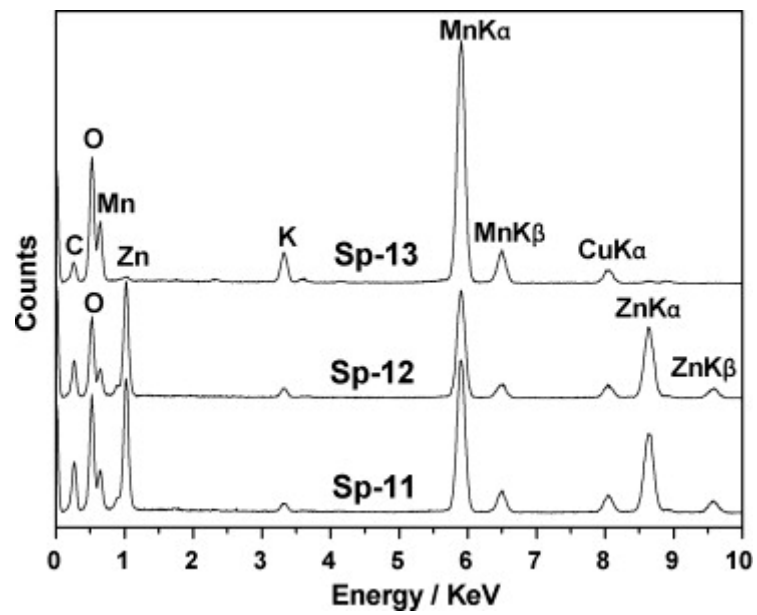


Fig. 7.

XRD pattern of the B_4C (5 wt.%) added MnO_2 (a) before discharge mixed with AB (acetylene black) and PVDF (binder), (b) discharged in the LiOH and (c) KOH electrolyte.

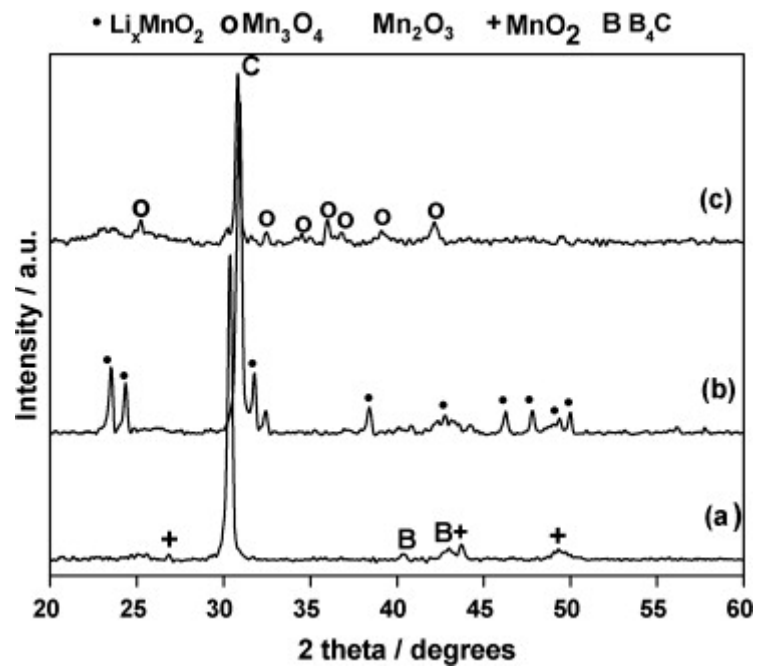


Fig. 8.

Multiple discharge–charge behavior of the B_4C (5 wt.%) added MnO_2 cathode using saturated aqueous $LiOH$ containing 1 mol l^{-1} of $ZnSO_4$ as the electrolyte. The capacity of the cell decreases upon prolonged cycling—cycle numbers are indicated.

