The objective of the proposed study is to use ANSTO’s transmission electron microscopy (TEM) and elastic recoil detection analysis (ERDA) combined with Rutherford back scattering (RBS). TEM and its associated techniques like HR-TEM (High resolution) and electron energy loss spectroscopy (EELS) are proposed to determine the lattice fringes and electron diffraction pattern with d-spacing corresponding to lithium intercalated manganese dioxide (MnO₂). ERDA technique is proposed to assess the possibility to measure surface-near elemental depth profiles of Li, Zn, Mn etc in one single beam shot in a discharged (Li intercalated) MnO₂ cathode material.

The great advantage of SIMS technique is the principle ability to measure these elemental depth profiles simultaneously. However, quantifying the trace elements is challenging. In this regard, ERDA combined with RBS are the complimentary techniques. It is a powerful and relatively simple analytical technique by measuring intensities of characteristic X-ray lines one can determine concentrations of almost all elements i.e. Li, Mn, Zn and C in the discharged MnO₂ sample down to approximately 10 ppm (parts per million). Successful measurements would offer the possibility to use the analytical results to conclude the amount of lithium intercalated into MnO₂.

The national benefit of this research derives from an improved understanding of the mechanism involved in aqueous batteries. This greater understanding will facilitate the development of an environmental friendly rechargeable alkaline battery.

PROGRESS REPORT and RESEARCH OUTCOMES (In addition to a discussion of your research results please indicate the value of any other funding generated by AINSE support for this project and the resulting benefits, if any, to the Australian community):

In this AINSE Project, I have carried out work along with ANSTO scientists M. Blackford and G. Thorogood, on boron carbide (B₄C) modified MnO₂ cathodes to investigate its suitability for better rechargeability, in comparison to that of our previous work on Bi₂O₃ and CeO₂ modified cell. Boron-doping into graphite to improve the discharge capacity of the graphite electrode in a lithium battery using non-aqueous solvent as electrolyte 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. Herein, boron carbide (B₄C) has been used in as an additive to MnO₂ cathode material for the first time. The objective of this project 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.

The obtained results i.e. enhanced discharge capacity indicates that boron atoms promote lithium intercalation during the electrochemical process and improved the performance of the Zn|MnO₂|LiOH battery.

Upon accessing the following instrumentation times at ANSTO; 4 days on TEM, 2 days on metallographic specimen preparation and 2 days on XRD - we have obtained very useful results and this work resulted in the form of two publications and submitted to the journals. Further to this, I would like to perform a more detailed work on the lithium insertion/extraction mechanism on various weight percent of additives in LiOH and KOH electrolytes, for which I am in need of additional 2 days of TEM access time. Could you be kind enough to approve this? Please be noted that I haven’t used the Time of Flight Spectrometer yet, which I will be using in the month of August to depth profile my lithium interacted samples.
1. Electrochemical discharge characteristics in LiOH electrolyte (work done at home institution)

Figure 1 compares the discharge characteristics of the B₄C modified MnO₂ with Zn as an anode. The discharge capacity of the B₄C modified MnO₂ to ≤ 7 wt. % is increased significantly as compared with the pure MnO₂ (0 wt % additive), i.e. from 145 mAh/g 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. It is also found that the voltage profiles for all B₄C modified MnO₂ cathodes are lower than pure MnO₂. 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. Boron has three valence electrons, one electron more than manganese, therefore when added into a MnO₂ host lattice, acts as an electron donor. During the discharge process, when lithium is inserted into the manganese host the additive boron carbide acts as an electron acceptor, accepting its 2s electron to the manganese host. This suggests the presence of boron weakens the chemical bond between the lithium intercalated MnO₂ (LiₓMnO₂) and the B₄C modified MnO₂ compared to the pure MnO₂. The strength of the bond determines the chemical potential of the MnO₂ which in turn determines the cell voltage. As a result, the potential of the B₄C modified MnO₂ could be decreased relative to the unmodified cell (in Fig. 1).

2. Material Characterization (work done at ANSTO)

In order to elucidate the role of boron carbide in the LiOH electrolyte, the discharged MnO₂ was characterised using ANSTO’s TEM, EDS and XRD techniques and compared this with before discharge material. Bright field TEM images of the boron carbide (5 wt. %) modified MnO₂ before discharge are shown in Fig. 2. The term “sp” on figures indicates the position from which EDS spectra were recorded. Fig. 2a shows the MnO₂ before discharge is composed of sub micron clumps of individual crystals. Selected area electron diffraction confirmed the MnO₂ to be crystalline. Boron carbide (B₄C) particles were scarce and tended to be several microns in size with MnO₂ clumps adhering to the surface (Fig. 2b). This indicates that the boron carbide is not homogenously mixed within the MnO₂ cathode material.
**Fig. 2** TEM images of the B₄C modified MnO₂ before discharge showing (a) bright field image of MnO₂ clumps and (b) large particle of B₄C (sp3) with small MnO₂ clumps attached (sp4-6). Term “sp” refers to EDS spectra.

Bright field TEM images of the B₄C modified MnO₂ cathode after the first discharge cycle in LiOH electrolyte are shown in Figure 3. 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. 3b) and corresponding EDS spectra 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. The presence of boron carbide appears to have increased the intercalation process. The intercalation mechanism is further evidenced by X-ray diffraction analysis on the material before and after the discharge process.

**Fig. 3** TEM image of the B₄C (5 wt. %) modified MnO₂ discharged in LiOH solution (a) bright field image of clustered MnO₂ and its magnified image (b) showing crystalline particles of Zn oxide (sp3) and Mn oxide (sp4).

**Fig. 4** XRD pattern of the B₄C (5 wt. %) modified MnO₂ (a) before discharge mixed with AB (Acetylene black) and PVDF (binder), (b) discharged in the LiOH electrolyte.
Figure 4 a-b show x-ray diffraction patterns of the B$_4$C modified MnO$_2$ cathode before and after discharge in LiOH electrolyte. The before discharge material (Fig. 4a) shows the characteristic peaks of MnO$_2$ (+) and boron carbide (B) as quoted in the JCPDS cards. The cathode discharged in LiOH electrolyte (Fig. 4b) 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 MnO$_2$ (+) are replaced by those of a new phase corresponding to a lithium intercalated MnO$_2$ (Li$_x$MnO$_2$) (●) with a minor phase formation of Mn$_2$O$_3$ (□). Based on this, it is proposed that reduction of Mn occurs via intercalation of lithium. The presence of boron carbide appears to have increased the intercalation process.

To investigate the rechargeability, 5 wt. % B$_4$C added cell was tested for multiple cycles and their results are compared in Fig. 5. 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 cycles, corresponding to a 38% loss in capacity. Although the material is rechargeable the fade in capacity is significant on cycling for this B$_4$C modified MnO$_2$ cell in comparison to that of Bi$_2$O$_3$ and CeO$_2$ modified cell.

**Fig. 5** Multiple discharge-charge behavior of the B$_4$C (5 wt. %) modified 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.

<table>
<thead>
<tr>
<th>Signature of Investigator preparing the report for</th>
<th>Proj: AINGRA09115P</th>
</tr>
</thead>
<tbody>
<tr>
<td>After signing this report please fax this page with your signature for our files</td>
<td>Date: 11 May 2009</td>
</tr>
</tbody>
</table>

**PUBLICATIONS / REPORTS arising as a result of your work.**

Please provide references in the following format Relevant AINSE Grant no(s); paper; Journal, Conference Proceedings or Book Title; Volume, ISSN/ISBN no., or Book/Publisher; Page numbers. Put an (s) to indicate that AINSE support was acknowledged and a (c) to indicate that AINSE has been provided with a copy.

2. M. Minakshi, M. G. Blackford, “Electrochemical characteristics of B$_4$C or BN added MnO$_2$ cathode material for alkaline Batteries” Submitted to a journal.
PhD STUDENTS  For each student involved with the project, please indicate the date or anticipated date of conferment of a PhD or other award, and give the title of the thesis.

N/A.