ELECTROCHEMISTRY OF CATHODE MATERIALS IN
AQUEOUS LITHIUM HYDROXIDE ELECTROLYTE

THIS THESIS IS PRESENTED FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY OF MURDOCH UNIVERSITY, WESTERN AUSTRALIA

BY

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M.Sc., M.Phil.,
2006
I declare that this thesis is my own account of my research and contains as its main content work which has not previously been submitted for a degree at any tertiary educational institution.

Minakshi Manickam

May 2006
Abstract

Electrochemical behavior of electrolytic manganese dioxide (EMD), chemically prepared battery grade manganese dioxide (BGM), titanium dioxide (TiO₂), lithium iron phosphate (LiFePO₄) and lithium manganese phosphate (LiMnPO₄) in aqueous lithium hydroxide electrolyte has been investigated. These materials are commonly used as cathodes in non-aqueous electrolyte lithium batteries. The main aim of the work was to determine how the electroreduction/oxidation behavior of these materials in aqueous LiOH compares with that reported in the literature in non-aqueous electrolytes in connection with lithium batteries. An objective was to establish whether these materials could also be used to develop other battery systems using aqueous LiOH as electrolyte.

The electrochemical characteristics of the above materials were investigated by subjecting them to slow scan cyclic voltammetry and determining the charge/discharge characteristics of Zn/cathode material-aqueous LiOH batteries. The products of electroreduction/oxidation were characterized by physical techniques using X-ray diffraction (XRD), scanning electron micrography (SEM), X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), Thermogravimetric analysis (TG) and infra-red spectrometry (IR).

The reduction of $\gamma$-MnO₂ (EMD) in aqueous lithium hydroxide electrolyte is found to result in intercalation of Li⁺ into the host structure of $\gamma$-MnO₂. The process was found to be reversible for many cycles. This is similar to what is known to occur for $\gamma$-MnO₂ in non-aqueous electrolytes. The mechanism, however, differs from that for reduction/oxidation of $\gamma$-MnO₂ in aqueous potassium hydroxide electrolyte. KOH electrolyte is used in the state-of-art aqueous alkaline Zn/MnO₂ batteries. Alkaline
batteries based on aqueous KOH as the electrolyte rely upon a mechanism other than K⁺ intercalation into MnO₂. This mechanism is not reversible. This is explained in terms of the relative ionic sizes of Li⁺ and K⁺. The lithium-intercalated MnO₂ lattice is stable because Li⁺ and Mn⁴⁺ are of approximately the same size and hence Li⁺ is accommodated nicely into the host lattice of MnO₂. The K⁺ ion which has almost double the size of Li⁺ cannot be appropriately accommodated into the host structure and hence the K⁺ - intercalated MnO₂ phase is not stable.

Chemically prepared battery grade MnO₂ (BGM) is found to undergo electroreduction/oxidation in aqueous LiOH via the same Li⁺ intercalation mechanism as for the EMD. While the Zn/BGM- aqueous LiOH cell discharges at a voltage higher than that for the Zn/EMD- aqueous LiOH cell under similar conditions, the rechargeability and the material utilization of the BGM cell is poorer.

The cathodic behavior of TiO₂ (anatase phase) in the presence of aqueous LiOH is not reversible. In addition to LiTiO₂, Ti₂O₃ is also formed. The discharge voltage of the Zn/TiO₂- aqueous LiOH cell and material utilization of the TiO₂ as cathode are very low. Hence TiO₂ is not suitable for use in any aqueous LiOH electrolyte battery.

LiFePO₄ (olivine-type structure) as a cathode undergoes electrooxidation in aqueous LiOH forming FePO₄. However the subsequent reduction forms not only the original LiFePO₄ but also Fe₂O₄. Thus the process is not completely reversible and hence LiFePO₄ is not a suitable material for use as a cathode in aqueous battery systems.

LiMnPO₄ (olivine-type structure) undergoes reversible electrooxidation in aqueous LiOH forming MnPO₄. The charge/discharge voltage profile of the Zn/MnPO₄- aqueous LiOH cell, its coulombic efficiency and rechargeability are comparable to that of
the cell using $\gamma$-MnO$_2$. EMD and LiMnPO$_4$ both have the potential for use in rechargeable batteries using aqueous LiOH as the electrolyte. Recommendations for further developmental work for such batteries are made.
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Acknowledgements

The work presented in this thesis was carried out under the joint supervision of Professor Pritam Singh and Professor Stephen Thurgate. To them I extend my deepest sense of gratitude for their valuable, friendly guidance and helpful suggestions throughout the progress of the research and in preparation of this thesis. I am very grateful to Associate Professor Roland DeMarco, Curtin University of Technology for his discussions and help given.

I would like to extend my thanks to Kathryn Prince at ANSTO, without whom the SIMS work would not have been possible. I would especially like to acknowledge Ian Kelly for his friendly instruction and helpful advice while operating SIMS. Thanks are also due to David Mitchell at ANSTO for enabling me to have TEM spectra run at his premises.

I would also like to extend my sincere thanks to Dion Giles who helped me greatly in preparation of this thesis. I am also grateful to Touma Issa for his help with the project on numerous occasions.

I acknowledge with thanks the financial support from Murdoch University in the form of a postgraduate research scholarship and AINSE for a PGRA top up scholarship which funded access to ANSTO. Thanks also go to AINSE Scientific Secretary Dennis Mather and staff members Ben Thompson and Rhiannon Still.

I am also indebted to Doug Clarke, Tom Osborne, Ken Seymour, Stewart Kelly, Peter Fallon, and Kleber Claux at Murdoch University for their technical support in different aspects throughout the course of this study. I also wish to acknowledge John Orton, Sue Lawson, Lian Chan and MPS store staff at physical sciences, Murdoch University, who
provided help during my study. I wish to express my thanks to my fellow students for their fun and friendship.

Finally, my heartfelt thanks to my parents and my sister for their love, support and encouragement throughout all my years of study.
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Chapter 1

Introduction

With the rapid development of new electronic devices and the realization that fossil fuels are depleting fast, the demand for reliable batteries is rising. A large variety of batteries has been developed over the years. Some of such batteries and their characteristics are included in Table 1.1. An important concern is the environmental threat posed by the heavy metals used in many of today’s batteries, proposed or currently in use. Non-aqueous solvents in batteries also pose environmental problems. As society is becoming more aware of these problems, the desire for environmentally friendly battery components is growing.

A battery is a device that converts chemical energy contained in its active materials directly into electrical energy by means of an electrochemical oxidation-reduction (redox) reaction [1].
<table>
<thead>
<tr>
<th>Common name</th>
<th>Operating Voltage/V</th>
<th>Specific energy density /Wh.Kg⁻¹</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous alkaline electrolyte batteries</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nickel/cadmium</td>
<td>1.20</td>
<td>55</td>
<td>Electric vehicles, aerospace, consumer</td>
</tr>
<tr>
<td>Nickel/iron</td>
<td>1.20</td>
<td>60</td>
<td>Electric vehicles</td>
</tr>
<tr>
<td>Nickel/zinc</td>
<td>1.60</td>
<td>75</td>
<td>Electric vehicles</td>
</tr>
<tr>
<td>Nickel/metal hydride</td>
<td>1.20</td>
<td>65</td>
<td>Electric vehicles, aerospace, consumer</td>
</tr>
<tr>
<td>Nickel/hydrogen</td>
<td>1.50</td>
<td>60</td>
<td>Aerospace, electric vehicles</td>
</tr>
<tr>
<td>Edison (Fe/Ni oxide)</td>
<td>1.40</td>
<td>55</td>
<td>Energy storage</td>
</tr>
<tr>
<td>Zinc/manganese dioxide</td>
<td>1.4</td>
<td>80</td>
<td>Consumer</td>
</tr>
<tr>
<td>Zinc/air</td>
<td>1.1</td>
<td>110</td>
<td>Electric vehicles</td>
</tr>
<tr>
<td>Aqueous Acidic Electrolyte Batteries</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lead/acid</td>
<td>1.9</td>
<td>50</td>
<td>Electric vehicles, utility energy storage, consumer</td>
</tr>
<tr>
<td>Zinc/bromine (redox flow)</td>
<td>1.6</td>
<td>80</td>
<td>Utility energy storage</td>
</tr>
<tr>
<td>Zinc/chlorine</td>
<td>2.1</td>
<td></td>
<td>Energy storage</td>
</tr>
<tr>
<td>Silver-zinc</td>
<td>1.85</td>
<td></td>
<td>Military and space applications</td>
</tr>
<tr>
<td>Cadmium-zinc</td>
<td>1.40</td>
<td></td>
<td>Utility energy storage</td>
</tr>
<tr>
<td>Zinc/silver oxide (redox flow)</td>
<td>1.55</td>
<td>150</td>
<td>Aerospace, military</td>
</tr>
<tr>
<td>Molten Electrolyte Batteries</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium/sulphur</td>
<td>2.0</td>
<td>170</td>
<td>Electric vehicles, utility energy storage</td>
</tr>
<tr>
<td>Sodium/nickel chloride</td>
<td>2.4</td>
<td>140</td>
<td>Electric vehicles</td>
</tr>
<tr>
<td>Lithium/Iron disulphide</td>
<td>1.8</td>
<td>175</td>
<td>Electric vehicles</td>
</tr>
<tr>
<td>Lithium/Iron monosulphide</td>
<td>1.45</td>
<td>100</td>
<td>Electric vehicles</td>
</tr>
<tr>
<td>Non-aqueous Electrolyte Batteries</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lithium ion</td>
<td>4.0</td>
<td>285</td>
<td>Medical applications</td>
</tr>
<tr>
<td>Li/SOCl₂</td>
<td>3.6</td>
<td>400</td>
<td>High energy storage applications</td>
</tr>
<tr>
<td>Lithium/MnO₂</td>
<td>3.2</td>
<td>265</td>
<td>High energy storage applications</td>
</tr>
</tbody>
</table>
Batteries are classified as primary and secondary. In primary batteries, the electrode reactions are not reversible and the cells are therefore not rechargeable. After one discharge, primary batteries are discarded. In secondary batteries, the electrode reactions are reversible and hence the cells are rechargeable.

A battery comprises three major components as shown schematically in fig.1.1:

![Diagram of a battery](image)

**Fig. 1.1 Schematic diagram of the battery [2]**

The cathode (positive electrode) accepts electrons from the anode (negative electrode) through the external circuit and is reduced during the battery discharge reaction.

The electrolyte is an electronic insulator, but a good ionic conductor; its main function is to provide a transport medium for ions to travel from one electrode to the other. It also prevents short-circuiting by acting as a physical barrier between the electrodes.
A separator is needed to maintain an even spacing between the electrodes while blocking electronic current and passing the ionic current. Common separators are porous electronic insulators permeated by liquid electrolyte.

During cell discharge, electrons pass from the anode to the cathode through an external load of resistance $R_L$ and ions flow inside the cell to convert chemical energy into electrical energy as schematically illustrated in fig.1.2. The electronic current $I$ which is delivered by the cell to the external circuit is matched by the ionic current within the cell. Any leakage of electrons from anode to cathode within the cell reduces the current $I$ delivered by the cell.

![Diagram of electrochemical operation of a cell (discharge)](image)

**Fig. 1.2** Electrochemical operation of a cell (discharge)
During charging of the cell, electric current is forced in the opposite direction by an externally applied voltage to convert electrical energy back into chemical energy; oxidation takes place at the positive electrode and reduction at the negative electrode. A schematic diagram of a cell charge is shown in fig. 1.3.

![Schematic diagram of cell charge](image)

**Fig. 1.3** Electrochemical operation of a cell (charge)

For example electrode reactions of lead-acid battery are as follows [4]:

<table>
<thead>
<tr>
<th>Anode</th>
<th>Pb + H₂SO₄</th>
<th>⇌</th>
<th>PbSO₄ + 2H⁺ + 2e⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode</td>
<td>PbO₂ + H₂SO₄ + 2H⁺ + 2e⁻</td>
<td>⇌</td>
<td>PbSO₄ + 2H₂O</td>
</tr>
</tbody>
</table>

**Total cell reaction:** Pb + PbO₂ + 2H₂SO₄ ⇌ 2PbSO₄ + 2 H₂O  
Eq. [1.1]
The capacity of a cell is expressed as the total quantity of electricity involved in the electrochemical reaction and is defined in terms of coulombs or ampere-hours. The “ampere-hour capacity” of a battery is directly related to the quantity of the active materials which actually take part in the battery reaction.

The theoretical capacity expressed as coulombs or ampere hours of a battery system is based on the total quantity of the active materials which participate in the electrochemical reaction. It is calculated from the equivalent weight of the reactants. For example the theoretical capacity of the Li/MnO$_2$ is 285 mAh/g based upon Li as the limiting reagent [5]. The battery reaction is as follows

$$\text{Li} + \text{MnO}_2 \rightarrow \text{LiMnO}_2$$  Eq. [1.2]

Likewise for Zn/MnO$_2$ the theoretical capacity is 224 Ah/kg based on Zn or MnO$_2$. The theoretical energy density (Wh/Kg) is expressed as the specific theoretical capacity at the theoretical cell voltage.

The overall objective of this thesis is to study the electrochemical behavior of various materials in relation to their use as cathodes in aqueous LiOH electrolyte batteries. These materials include oxide compounds MnO$_2$, TiO$_2$ and phosphate compounds LiFePO$_4$, FePO$_4$, and LiMnPO$_4$ which are commonly used in lithium batteries using non-aqueous electrolytes. The main objective is to investigate whether reversible intercalation of Li$^+$ into the host structure of the above materials does occur in aqueous media similarly to that in non-aqueous electrolytes commonly used in lithium
batteries. If this mechanism were possible in aqueous media then these cathode materials could also be used in rechargeable batteries with aqueous electrolytes.

The aqueous secondary batteries could be very attractive for a range of applications because they would be fundamentally more safe and cost effective than non-aqueous lithium batteries. This is because, they do not use expensive flammable non-aqueous solvents. Furthermore the conductivities of aqueous solutions are higher than those of non-aqueous electrolyte solutions.
1.1 References


Chapter 2

Battery systems: Brief overview

2.1 Introduction

As noted in the previous chapter, a battery is an electrochemical cell which could be classified as primary (non rechargeable) or secondary (rechargeable), depending on its capability of being electrically recharged. Within this classification, other classifications are used to identify particular types or designs. A brief overview of some batteries is presented in Table. 2.1.

2.1.1 Primary batteries

The zinc-manganese dioxide battery is the most commonly known primary battery which dominates the primary battery market segment [1]. Leclanché invented the original cell in 1860. He used natural manganese dioxides – carbon black core cathode with aqueous zinc chloride-ammonium chloride electrolyte, contained in a zinc can [2]. An alternative version employs a zinc chloride electrolyte and a synthetic electrolytic manganese dioxide (EMD) with KOH as the electrolyte. It has a better performance than the original Leclanché cell. Over the years several other aqueous electrolyte primary batteries have been developed with the objective of having batteries which could deliver desired discharge characteristics appropriate for specific applications [3-4]. Some of these are listed in Table 2.1. Lithium batteries which can deliver high energy density and high voltage have been developed for applications which could not be serviced by aqueous electrolyte batteries. Since lithium is highly reactive, lithium batteries either are all solid-state or use non-aqueous electrolytes (Table 2.1).
# Table 2.1 Common Commercial Battery System [4]

<table>
<thead>
<tr>
<th>Common name</th>
<th>Nominal Voltage</th>
<th>Anode</th>
<th>Cathode</th>
<th>Electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>primary</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>leclanché (carbon-zinc)</td>
<td>1.5</td>
<td>zinc foil</td>
<td>MnO₂ (natural)</td>
<td>aq ZnCl₂-NH₄Cl</td>
</tr>
<tr>
<td>zinc chloride (carbon-zinc)</td>
<td>1.5</td>
<td>zinc foil</td>
<td>electrolytic MnO₂</td>
<td>aq ZnCl₂</td>
</tr>
<tr>
<td>alkaline</td>
<td>1.5</td>
<td>zinc powder</td>
<td>electrolytic MnO₂</td>
<td>aq KOH</td>
</tr>
<tr>
<td>zinc-air</td>
<td>1.2</td>
<td>zinc powder</td>
<td>carbon (air)</td>
<td>aq KOH</td>
</tr>
<tr>
<td>silver-zinc</td>
<td>1.6</td>
<td>zinc powder</td>
<td>Ag₂O</td>
<td>aq KOH</td>
</tr>
<tr>
<td>lithium-manganese oxide</td>
<td>3.0</td>
<td>lithium foil</td>
<td>treated MnO₂</td>
<td>LiCF₃SO₃ or LiClO₄&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>lithium-carbon monofluoride</td>
<td>3.0</td>
<td>lithium foil</td>
<td>CFₓ</td>
<td>LiCF₃SO₃ or LiClO₄&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>lithium-iron sulphide</td>
<td>1.6</td>
<td>lithium foil</td>
<td>FeS₂</td>
<td>LiCF₃SO₃ and/or LiClO₄&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td><strong>rechargeable</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>lead acid</td>
<td>2.0</td>
<td>lead</td>
<td>PbO₂</td>
<td>aq H₂SO₄</td>
</tr>
<tr>
<td>nickel-cadmium</td>
<td>1.2</td>
<td>cadmium</td>
<td>NiOOH</td>
<td>aq KOH</td>
</tr>
<tr>
<td>nickel-metal hydride</td>
<td>1.2</td>
<td>MH</td>
<td>NiOOH</td>
<td>aq KOH</td>
</tr>
<tr>
<td>lithium ion</td>
<td>4.0</td>
<td>Li(C)</td>
<td>LiCoO₂</td>
<td>LiPF₆ in non-aqueous solvents&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>rocking chair battery</td>
<td>4.0</td>
<td>Li₃C₆</td>
<td>LiNiO₂</td>
<td>DME in EC-PC solvents&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td><strong>specialty</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nickel-hydrogen</td>
<td>1.2</td>
<td>H₂ (Pt)</td>
<td>NiOOH</td>
<td>aq KOH</td>
</tr>
<tr>
<td>lithium-iodine</td>
<td>2.7</td>
<td>Li</td>
<td>I₂</td>
<td>LiI</td>
</tr>
<tr>
<td>lithium-silver-vanadium oxide</td>
<td>3.2</td>
<td>Li</td>
<td>Ag₂V₄O₁₁</td>
<td>LiAsF₆&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>lithium-sulphur dioxide</td>
<td>2.8</td>
<td>Li</td>
<td>SO₂ (C)</td>
<td>SO₂-LiBr</td>
</tr>
<tr>
<td>lithium-thionyl chloride</td>
<td>3.6</td>
<td>Li</td>
<td>SOCl₂ (C)</td>
<td>SOCl₂-LiAlCl₄</td>
</tr>
<tr>
<td>lithium-iron sulphide</td>
<td>1.6</td>
<td>Li</td>
<td>FeS₂</td>
<td>LiCl-LiBr-LiF</td>
</tr>
<tr>
<td>magnesium-silver chloride</td>
<td>1.6</td>
<td>Mg</td>
<td>AgCl</td>
<td>seawater</td>
</tr>
</tbody>
</table>

<sup>a</sup> In non-aqueous solvents. Exact composition depends on the manufacturer, usually propylene carbonate-dimethyl ether for primary lithium batteries and ethylene carbonate with linear organic carbonates such as dimethyl carbonate, diethyl carbonate, and ethylmethyl carbonate for lithium ion cells.
Lithium batteries show higher energy density than aqueous electrolyte batteries [5-6]. The characteristics of some batteries are listed in Table 2.2. These batteries, however, have a lower rate capability because of the lower conductivity of the non-aqueous electrolyte and the low lithium cation transport rate. Commercial lithium primary batteries use cathodes like MnO₂, (CF)ₙ, FeS₂, and CuO [1, 7-9]. Typically, the electrolyte is lithium perchlorate in propylene carbonate-dimethyl ether (PC-DME) solvent [10-11]. The lithium-iodine system with a lithium iodide solid electrolyte is the all solid state battery.

<table>
<thead>
<tr>
<th>System</th>
<th>Open circuit voltage (OCV) / V</th>
<th>Theoretical faradic capacity (Ah.g⁻¹)</th>
<th>Energy density (W h. kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li/(CF)ₙ</td>
<td>3.1</td>
<td>0.86</td>
<td>2180</td>
</tr>
<tr>
<td>Li/CuO</td>
<td>2.2</td>
<td>0.67</td>
<td>1280</td>
</tr>
<tr>
<td>Li/FeS₂</td>
<td>1.8</td>
<td>0.89</td>
<td>1304</td>
</tr>
<tr>
<td>Li/MnO₂</td>
<td>3.0</td>
<td>0.31</td>
<td>1005</td>
</tr>
</tbody>
</table>

### Table 2.2 Characteristics of some primary lithium battery systems [1, 12]

#### 2.1.2. Secondary (rechargeable) batteries

Rechargeable cells generally have lower energy storage capability than primary cells. The additional requirements for rechargeability and long operation limit the choice of chemical systems and constructions to those that are more robust than for primary batteries. The lead acid battery dominates the rechargeable market [13]. In PbO₂ cells, in addition to lead and lead-oxide electrode, sufficient amounts of sulphuric acid and water
have to be provided for the cell reaction and the formation of battery electrolyte [13]. For ionic conductivity in the charged and discharged state, an excess of acid is necessary. Considering the limited mass utilization, and the necessity of inactive components such as grids, separators, cell containers etc., the practical value of specific energy is only \( \sim 25\% \) of the theoretical value for rechargeable batteries [14]. Because of the heavy electrode and electrolyte components used, the specific energy is low. Nevertheless, in the absence of any other reliable battery technology the lead acid system continues to serve a variety of applications ranging from automotive SLI (Starting, Lighting and Ignition) and motor power for forklift trucks and the like to stationary energy storage for uninterruptible power supplies [13-14].

Nickel-cadmium (Ni-Cd) is another commonly known secondary battery. It was the first small sealed rechargeable cell. In alkaline (KOH) electrolyte, the Cd negative electrode functions reversibly with Cd(OH)\(_2\) being the discharged product [15]. The Ni positive electrode is actually Ni(OH)\(_2\) which is able to reversibly de-insert/insert protons during charge/discharge. It has excellent low temperature and high rate capabilities. For a long time, it was the only battery available for power tools. The availability of stable hydrogen storage alloys provided the impetus for the creation of the nickel-metal hydride (Ni-MH) cell. The hydrogen storage alloy is a proton-inserting negative electrode material that replaced the environmentally harmful cadmium negative electrode in the Ni-Cd. The positive electrode and the electrolyte stayed the same. Ni-MH quickly replaced the Ni-Cd for electronic applications because of its significantly higher energy storage capability and somewhat lighter weight. Ni-MH has poor low temperature capability and
limited high-rate capability, but its higher energy density served to spur the development of the portable electronic device market [16].

![Energy density comparison of various batteries](image)

**Fig. 2.1** Energy density comparison of various batteries [41]

The lithium ion battery has significantly higher energy density [17] (fig. 2.1) than lead-acid, Ni-Cd and Ni-MH batteries. It is now the battery of choice for portable electronic devices and is challenging other battery technologies for hybrid vehicle applications. The development of this battery required extensive development of cathode and anode materials. The chemical reactivity constraints also necessitated development of suitable non-aqueous electrolytes. Extensive literature relating to the development of this battery is available [13-17]. The most successful rechargeable lithium battery is the “rocking-chair battery”. This battery uses an anode and a cathode, both of which can
reversibly intercalate Li⁺ ions during charge/discharge cycles. A schematic diagram of its operation is shown in fig. 2.2.

![Schematic diagram of discharge and charge processes in a “rocking-chair” lithium ion rechargeable battery](image)

**Fig. 2.2** Schematic diagram of discharge and charge processes in a “rocking-chair” lithium ion rechargeable battery [103]

The battery uses “intercalation” or “insertion” or “host guest” type electrodes proposed by Whittingham [4] and the significant improvements on their performance was made by Goodenough et al and others [18]. Most of the intercalation materials are transition metal oxides or chalcogenides with stable crystal lattices, and their layer or tunnel structures provide the pathways for guest ions such as lithium ions to diffuse. By injecting or extracting electrons, the redox reactions occur on the host lattice while mobile guest ions intercalate into or deintercalate from the host matrix to compensate for
regional electroneutrality. During the whole intercalation/deintercalation cycle, there are no faradic charges in the guest ion. The nickname “rocking chair battery” [19-21, 28] was given to such a devices because they use dual intercalation electrodes, the working principle of which is schematically depicted in fig. 2.3.

![Charge and Discharge Mechanism of a Li ion Battery](image)

**Fig. 2.3** Charge and discharge mechanism of a Li ion battery [19]

The most commonly used anode which is commonly used in a “rocking-chair” lithium battery is graphite. Its Fermi energy is only about 0.5 eV below that of Li. Lithium can be inserted reversibly into graphite to form Li_xC_6, which is schematically shown in fig. 2.4.
Fig. 2.4 Schematic illustration of the insertion and extraction process of lithium ion between the layered structure (positive electrode; LiCoO₂) and the hexagonal structure (negative electrode; LiₓC₆) [19].

The anode reaction is

\[
\text{LiC}_6 \underset{\text{discharge}}{\xrightarrow{\text{charge}}} x \text{Li}^+ + x e^- + \text{Li}_{1-x}C_6 \quad \text{Eq. [2.1]}
\]

The research and commercialization of cathode materials for the “rocking-chair” battery centred on layered compounds which have an anion close-packed or almost close-packed lattice in which alternate layers between the anion sheets are occupied by a redox-active transition metal. Lithium ion could then insert into the essentially empty remaining layers. This is exemplified by LiₓTiS₂ [22] LiCoO₂ [23], LiNi₁₋ₓCoₓO₂ [24], LiNiₓMnₓCo₁₋₂ₓO₂ [25]. The spinels, e.g. LiMn₂O₄ [26], may be considered as a special case where the transition-metal cations are ordered in all layers.

The possible cathode materials for 4 V Li-ion battery are LiCoO₂, LiNiO₂, LiMn₂O₄ and Li(NiₓCo₁₋ₓ)O₂ (Table 2.3). Their voltage profiles are shown in fig. 2.5.
Table 2.3 Characteristics of several oxide cathodes in lithium batteries [27]

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Structure</th>
<th>Theoretical Capacity (mAh.g(^{-1}))</th>
<th>Observed Capacity (mAh.g(^{-1}))</th>
<th>Voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO(_2)</td>
<td>Layered</td>
<td>274</td>
<td>&gt; 135</td>
<td>3.6</td>
</tr>
<tr>
<td>LiNi(<em>{0.5})Co(</em>{1.5})O(_2)</td>
<td>Layered</td>
<td>275</td>
<td>&gt; 185</td>
<td>3.6</td>
</tr>
<tr>
<td>LiNiO(_2)</td>
<td>Layered</td>
<td>275</td>
<td>&gt; 160</td>
<td>3.6</td>
</tr>
<tr>
<td>LiMn(_2)O(_4)</td>
<td>Spinel</td>
<td>148</td>
<td>&gt; 120</td>
<td>3.8</td>
</tr>
<tr>
<td>LiMnO(_2)</td>
<td>Layered</td>
<td>285</td>
<td>&gt; 190</td>
<td><del>2.8</del>3.4</td>
</tr>
</tbody>
</table>

Fig. 2.5 Voltage versus a Li anode for layered Li\(_{1-x}\)CoO\(_2\), Li\(_{1-x}\)NiO\(_2\) and spinline Li\(_{1-x}\)Mn\(_2\)O\(_4\) [27]
LiCoO$_2$ [23, 28] is now utilized in commercial battery cells and shows very reliable reversibility. However, because of the toxicity and high price of cobalt, alternatives are needed.

The Li-Ni-O [29] system shows very high capacity at first, but its recyclability is extremely bad. Layered LiMnO$_2$ systems are promising candidates as cathode materials because of their high theoretical capacity (285 mAh/g) [30]. Table 2.3 lists characteristics of these materials. Spinels like LiMn$_2$O$_4$, orthorhombic LiMnO$_2$, or rock salt Li$_2$MnO$_3$ are also considered.

Layered manganese oxides transform to spinel phases upon electrochemical cycling. These are associated with the Jahn-Teller distortion. The appropriate ion size and the variable valence of transition metals make them favorites for formation of spinel-oxide structures with a cubic space group Fd3m. The general composition of a spinel structure [31] is AB$_2$O$_4$ (fig. 2.6), where A is the metal ion with a +2 valence and B is a metal ion with a +3 valence, with the O- ions forming an fcc lattice. Cations A can reside in the tetrahedral site 8a and B in the octahedral sites 16c and 16d. Lithium ions are preferentially accommodated in the tetrahedral site 8a in LiMn$_2$O$_4$ cathode material. Table 2.4 lists the open-circuit voltages of the cathode material at different levels of lithiation. Dependent upon the level of lithiation in LiMn$_2$O$_4$, the discharge capacity varies but is quite high which has led to advanced developments towards its application in lithium ion cells and has been extensively developed by Bell core labs [33-35] and reviewed by Thackeray et al [36-37].
**Fig. 2.6** Spinel structure [103]

**Table 2.4** Electrode characteristics of lithium manganese oxide spinel type compounds [32]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Insertion range</th>
<th>Voltage vs. Li (V)</th>
<th>Calculated capacity (mAhg(^{-1}))</th>
<th>Observed capacity (mAhg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(_x)Mn(_2)O(_4)</td>
<td>(x = 0-1)</td>
<td>4</td>
<td>148 at (x = 1)</td>
<td>140</td>
</tr>
<tr>
<td></td>
<td>(x = 1-2)</td>
<td>3</td>
<td>143 at (x = 2)</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td>(x = 2-2.5)</td>
<td>1.5</td>
<td>75 at (x = 2.5)</td>
<td>74</td>
</tr>
</tbody>
</table>

34
The electrochemical lithium intercalation in Li$_x$Mn$_2$O$_4$ in the range X = 1-2 proceeds by a two-phase reaction of cubic LiMn$_2$O$_4$ / tetragonal Li$_2$Mn$_2$O$_3$ at 3 V vs. Li. Reduction of manganese below Mn$^{3.5+}$ leads to a Jahn-Teller distortion of MnO$_6$ octahedron, which is the reason for second phase nucleation. This distortion results in a host lattice expansion of 12 % along the tetragonal c-axis. Only displacive changes in host lattice occur and the host of Mn$_2$O$_4$ remains intact. But the two-phase segregation and the 12% anisotropic expansion result in a rather fast fading of electrode capacity [32]. Besides, one of the major problems hindering the development of this material is the loss of capacity with extensive cycling, particularly at elevated temperatures [38].

Following the discovery of oxide-based ion intercalation materials, a technological breakthrough occurred, using phosphates as cathode materials in rechargeable non-aqueous lithium batteries. This battery utilizes natural, phosphate-based cathode material and offers the greatest combination of energy, cost, safety and environmental characteristics. In this context, Nasicon structure (Na Super-Ionic conductor), fig. 2.7, Na$_{1+x}$ Zr$_2$ (Si$_x$P$_{3-x}$)O$_{12}$ (0 < X < 3) having the highest alkali ion conductivity at room temperature among various crystalline compounds are appealing [18, 39-40]. This structure (Nasicon), because of its rather freely designed three-dimensional network, is able to accommodate other M$^+$ ions (Li$^+$, K$^+$, Ag$^+$) instead of Na$^+$, whereas Zr$^{4+}$ can be substituted by Ti$^{4+}$, Sc$^{3+}$, Fe$^{3+}$, Al$^{3+}$, Y$^{3+}$, La$^{3+}$ [40-41]. This host framework provides interstitial space for guest atoms, which are mobile,
Fig. 2.7 Schematic representation of the Nasicon type structure [103]

and the concentration of which may change along with the oxidation state of the host lattice atoms.

The structure shown above in fig. 2.7, consists of a 3-D framework of PO₄ tetrahedra sharing corners with MO₆ octahedra and a 3-D linked interstitial space occupied by A ions: Type I sites (6b) situated between two ZrO₆ octahedra along the c-axis with a distorted octahedra coordination and Type II sites (18c) located between the ribbons (perpendicular to the c-axis) with a trigonal prismatic coordination. The ribbons are connected by PO₄ tetrahedra along the a-axis. Nasicon belongs to the class of NZP (NaZr₂(PO₄)₃) [40], as represented by the crystallographic formula, (Mᵢ) (Mᵢi)Zr₂(PO₄)₃ [41]. The Mᵢ site is at first fully occupied in the NaZr₂(PO₄)₃, the Mᵢi site being empty.
When the Na (or) Li content is increased by the substitution of elements of lower valence than M$^{4+}$, the M$_{II}$ site is filled partially [40-41].

The transition metal intercalation compounds have open structures capable of accommodating guest ions and a flexible electronic structure which can accommodate donated electrons and provide sufficient ionic and electronic conductivity. These properties result in a number of low-energy sites for guest ions within the lattice and the potential for high capacity lithium ion intercalation which occurs reversibly according to Eq. 2.2.

$$\text{Li}_x\text{Zr}_2(\text{PO}_4)_3 + e^- \rightarrow \text{Li}_{1+x}(\text{Zr}^{4+/3+})_2(\text{PO}_4)_3 \quad \text{(reduction) Eq. [2.2]}$$

The compounds shown in Table 2.5 are lithium transition metal phosphate cathode materials. These compounds have a rhombohedron unit cell of the R3-C space group at

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Structure</th>
<th>Redox couple</th>
<th>Voltage (V)</th>
<th>Observed capacity (mAh.g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$NaV$_2$(PO$_4$)$_3$</td>
<td>Nasicon</td>
<td>V$^{4+/3+}$</td>
<td>3.6</td>
<td>180</td>
</tr>
<tr>
<td>Li$_3$Fe$_2$(PO$_4$)$_3$</td>
<td>Nasicon</td>
<td>Fe$^{3+/2+}$</td>
<td>2.6</td>
<td>110</td>
</tr>
<tr>
<td>LiNa$_3$FeV(PO$_4$)$_3$</td>
<td>Nasicon</td>
<td>V$^{3+/2+}$</td>
<td>1.9</td>
<td>140</td>
</tr>
</tbody>
</table>

Table 2.5 Relative energy of the redox couples in materials with Nasicon framework [42]

room temperature, as shown in fig. 2.8. The black circles show the position of the Li atom in the (M$^{4+}$)$_2$ (PO$_4$)$_3$ framework.
**Fig. 2.8** Li(M^{4+})_2 (PO_4)_3 - NASICON structure showing the positions of Li atoms within the (M^{4+})_2 (PO_4)_3 framework [42, 103]

All the cathode materials discussed above are used in lithium batteries with non-aqueous electrolytes containing dissolved Li ions. The mechanisms through which these cathode materials undergo redox reactions in non-aqueous electrolyte are almost well characterized as far as their use in a lithium battery is concerned. The focus of the work described in this thesis is to explore whether Li^+ non-aqueous electrolyte could be replaced with an aqueous lithium hydroxide electrolyte particularly when the most commonly available cathode materials such as MnO_2, TiO_2, LiFePO_4, FePO_4 and LiMnPO_4 are used. Obviously, lithium metal or other types of lithium-containing anodes cannot be combined with these cathode materials in aqueous electrolyte systems. However, understanding of their electrochemical behavior in aqueous LiOH media might lead to development of aqueous rechargeable batteries which may have more attractive
features than are currently available. It could open up a new field of rechargeable batteries. A review of cathode materials of interest to the work described in this thesis is presented in section 2.2.1.

2.2 Review of cathode materials

2.2.1 Manganese dioxide as cathode material

Ever since 1866, when George Leclanché invented the galvanic cell, MnO₂ has been the principal cathode constituent in dry cells. Today it is used in alkaline, zinc chloride, Leclanché, magnesium and aluminium primary batteries as well as alkaline secondary batteries [1].

The Zn/MnO₂ cells are now well developed [43]. The MnO₂ electrode has been extensively reviewed [44-50]. In 1974 Kordesch [51] brought together for the first time the developments in both acidic and alkaline Zn/MnO₂ “dry” cells. The development of primary batteries has received further attention from Cahoon and his co-workers [52-53] and from Tye et al [54]. Several volumes [55-57] covering the investigations of prominent workers in the field are also available. Kozawa [58] briefly reviewed the properties of MnO₂ in a typical solid-phase redox system. Kordesch and Gsellmann [59] reviewed the alkaline Zn/MnO₂ cell. The manufacture of MnO₂ has been reviewed by Koshiba [60], Braker [61], Kobayashi and Kozawa [62] and Preisler [63]. Buzowa and Sobolev [64] discussed the structure, specific surface area, water content and electrical conductivity of MnO₂.

Tetravalent manganese dioxide occurs in more than 15 allotropic forms, of which only a few are useful for batteries [65-66]. Manganese dioxide used in batteries are
broadly classified into three groups according to their origin – i.e. natural manganese dioxide (NMD), chemical manganese dioxide (CMD), and electrolytic manganese dioxide (EMD) [67-69].

NMD is a natural ore chosen for its high content of battery-active MnO₂. It is not a single stoichiometric MnO₂ but, rather, a mixture of up to 10-20 different manganese oxide minerals [70] that have widely differing battery activities. CMD is synthesized by processes that include precipitation and chemical oxidation of manganese containing solutions or compounds. EMD is synthesized by electrochemical deposition at the anode from aqueous solutions of manganese salts, usually the sulphate [71].

The three battery-active classes of MnO₂ have some crystal similarity. CMD and EMD usually are γ-MnO₂ and the closely related ε-MnO₂ crystal classes. NMD’s usually contain natural γ-MnO₂ as a major and most important component. The γ-MnO₂ and ε-MnO₂ are non-stoichiometric and contain up to ~ 4% structural water. They are represented by the chemical formula MnOₓ·mH₂O, where x = 1.92-1.98. Thus, battery manganese dioxides are not strictly “MnO₂” although they are generally given this shorthand designation.

Despite crystal similarities, NMD, CMD and EMD exhibit different physical and electrochemical properties. NMD gives cell performance that is greatly inferior to that of the two synthetic forms. EMD exhibits the greatest battery activity for most applications [72].

The electrochemically active form of MnO₂ (EMD) is prepared by electrodeposition from a very acidic MnSO₄ bath at ~ 95° C and is often referred to as γ-MnO₂ [71]. The nomenclature of what constitutes γ-MnO₂ is not crisp, as described
below, but it is commonly thought of as an intergrowth of pyrolusite in a ramsdellite (fig. 2.9) phase with varying degrees of micro twinning. Pyrolusite, also known as β-MnO₂, is the stable form of MnO₂ at ambient conditions and has the tetragonal rutile structure. Ramsdellite has orthorhombic symmetry and has higher electrochemical activity than pyrolusite.

![Diagram](image)

**Fig. 2.9** Schematic diagram of the (a) P: pyrolusite (b) R: ramsdellite and (c) γ -MnO₂, an inter growth between ramsdellite (R); Mn (IV) sites, and pyrolusite (P); Mn (III) sites, shown in (001) plane [50].

The EMD material invokes the “2x1 (empty) tunnels” present in polyhedra-based crystal models of ramsdellite to provide the enhanced electrochemical activity of ramsdellite compared to pyrolusite, which contains only “1x1 tunnels”; in this view, proton transport
during electrochemical discharge occurs much more readily within the 2x1 tunnels of ramsdellite than in the 1x1 tunnels of pyrolusite, as shown in fig. 2.9. EMD consists of a hexagonal close-packed lattice of $O^{2-}$ ions in which half the octahedral sites are filled, almost at random by Mn$^{4+}$ ions, implying that some face-shared [MnO$_6$] octahedra may occur in EMD [73-74]. EMD ($\gamma$-MnO$_2$) is highly complex in its chemical composition as well as in its crystallographic structure.

Among the different models proposed to account for the behavior of $\gamma$-MnO$_2$ for a practical battery system [75], Ruetschi and Giovanoli [76] in 1988 proposed a cation vacancy model for MnO$_2$ prepared by electrodeposition. The model [76] assumes that the oxygen sub-lattice is complete (although some OH$^-$ ions substitute for oxygen for charge compensation) and that vacancies occur only on the manganese sub-lattice. The two types of cation defects that were proposed are: (1) a change of the oxidation state from Mn$^{4+}$ to Mn$^{3+}$ and (2) a manganese cation vacancy. Protons associated with the first defect type are called Coleman protons, while protons associated with the second one are Ruetschi protons. In this lattice-vacancy model of $\gamma$-MnO$_2$, it is considered that

1. Each manganese ion in the MnO$_2$ structure is octahedrally co-ordinated to six nearest oxygen ions, and each oxygen ion is co-ordinated to three nearest manganese ions. The MnO$_6$ octahedra are arranged in the crystal as to share edges and corners. Since the ionic radius of O$^{2-}$ ions (1.40 Å) is much larger than that of Mn$^{4+}$ ions (0.53 Å) the lattice resembles a dense packing of O$^{2-}$ ions, with the small Mn$^{4+}$ ions orderly arranged in the edge-shared MnO$_6$ octahedral chains between O$^{2-}$ layers [77]. This is the usual crystallographic description.
2. In this structure, a fraction of the Mn\(^{4+}\) ions are missing in the Mn\(^{4+}\) sub-lattice. Each empty Mn\(^{4+}\) site is, for charge compensation, coordinated to four hydrogen atoms, the latter being present in form of four OH\(^{-}\) ions. The OH\(^{-}\) ions replace O\(^{2-}\) in the lattice without significant volume change of the unit cell, the ionic radii of O\(^{2-}\) and OH\(^{-}\) being very similar [78]. Normal unit cell parameters are thus maintained.

3. A further fraction of the Mn\(^{4+}\) ions is replaced by Mn\(^{3+}\). For each Mn\(^{3+}\) present, one proton is introduced for charge compensation. These hydrogen atoms (protons) in the form of OH\(^{-}\) ions, replacing O\(^{2-}\) in the lattice.

4. Thus the lattice is composed of O\(^{2-}\), OH\(^{-}\), Mn\(^{4+}\) and Mn\(^{3+}\) ions and Mn vacancies. All the structural water is present in the form of OH\(^{-}\) ions, associated with either Mn vacancies, or Mn\(^{3+}\) ions.

The \(\gamma\)-MnO\(_2\) can be described by the chemical formula

\[
\text{Mn}^{4+}(1-\text{Y} \cdot \text{Z}) \text{Mn}^{3+}(\text{Z}) \text{O}^{2-}(2 \cdot \text{Y} \cdot \text{Z}) \text{OH}^{(4 \cdot \text{Y} \cdot \text{Z})}
\]

where \(Y\) is the cation vacancy fraction and \(Z\) is the fraction of Mn\(^{3+}\) ions replacing Mn\(^{4+}\) in the manganese sub-lattice.

The electrochemical reactions that take place at the manganese dioxide electrode in aqueous cell [79] during the discharge process of a battery corresponding to the insertion of H\(^{+}\) can then be described by the following Eq. [2.3-2.5].

\[
X < 1 - \text{Y} \cdot \text{Z} \\
(1 - \text{Y} \cdot \text{Z}) \text{Mn}^{3+}(\text{Z}) \text{O}^{2-}(2 \cdot \text{Y} \cdot \text{Z}) \text{OH}^{(4 \cdot \text{Y} \cdot \text{Z})} + \text{XH}^{+} + \text{Xe}^{-} \rightarrow \text{Mn}^{4+}(1 - \text{Y} \cdot \text{Z} \cdot \text{X}) \text{Mn}^{3+}(\text{Z} + \text{X}) \text{O}^{2-}(2 \cdot \text{Y} \cdot \text{Z} - \text{X}) \text{OH}^{(4 \cdot \text{Y} + \text{Z} \cdot \text{X})} [2.3]
\]

e\(^{-}\) representing an electron and \(X\) the number of proton. Eq. [2.3] is generally reported in the literature [79] in the following simplified way
\[ \gamma\text{-MnO}_2 + XH^+ + Xe^- \rightarrow \text{MnO}_{(2-x)Y}OH_x \]  \[2.4\]

For \( X > 1-Y-Z \)

\[ \text{Mn}_{(1-Y)Y}O_{(1+Y)Y}OH_{(1+Y)Y} + XH^+ + Xe^- \rightarrow \text{mixture of } [(\text{Mn}_3\text{O}_7 \text{ or } \text{Mn}_3\text{O}_4) + \text{Mn} (\text{OH})_2] \]  \[2.5\]

The products of the materials produced after discharge in Eq. [2.5] is known to be electrochemically inactive thus the material is suitable only for primary batteries in aqueous solutions. The mechanism for the electrochemical reduction/oxidation of \( \text{MnO}_2 \) in non-aqueous media has been investigated by several researchers [17-19]. The mechanism for the electrochemical reduction/oxidation of \( \text{MnO}_2 \) in non-aqueous media has been investigated by several researchers [17-19]. The mechanism of discharge/charge cycles for \( \text{MnO}_2 \) has been proposed to be quite different from that in aqueous KOH media.

In the non-aqueous lithium cells during discharge, lithium ions are inserted into the vacant sites while the \( \text{Mn}^{4+} \) ions are replaced by \( \text{Mn}^{3+} \) ions, which explains the electrochemical behavior of \( \gamma\text{-MnO}_2 \) associated with the discharge of lithium-MnO\(_2\) batteries. The electrochemical reaction for non-aqueous lithium cells is generally written as

\[ \text{MnO}_2 + \text{Li}^+ + e^- \rightarrow \text{LiMnO}_2 \]  \[2.6\]

2.2.2 Titanium dioxide as cathode material

Titanium (Ti) has become available as a commercial metal only since World War II, and, at low price, a decade later. As a recent arrival, Ti has not been extensively utilized as a reactant or energy-supplying material in batteries, despite its advantageous
properties: its low weight-density and potential for high energy density. Reviews of its
electrochemical behavior in aqueous, non-aqueous and molten salt media are available in
the literature [80-82].

Even though the physical, mechanical and electrochemical properties of titanium
are attractive as an active material in battery systems no papers or patents on Ti batteries
of any kind have been published since late 1973 [83]. Before that, articles published [84-
86] dealt only with recommendations for the use of Ti in the grids of storage batteries and
the possibility of using Ti as a battery negative in primary cells.

Titanium hydride, the composition of which is close to the formula TiH₂, is inert
to air, water and most acids and decomposes slowly at 400°C [85]. The heat of formation
is only –144 kJ mol⁻¹. It is commercially available and has been shown to work as a good
cathode material in lithium batteries [85].

Titanium sulphides, along with sulphides of other transition metals (Nb and Ta),
have been proposed as cathodic materials in non-aqueous lithium cells [87]. The cycling
behavior of cells with NbS₃, NbSe₃, TaSe₃ and TiS₃ as cathode has been reported [88]
and the prospects of such batteries have been discussed in a literature [89]. During the
studies of lithium non-aqueous cells with TiS₃ and NbSe₃ cathodes, it was found that,
whereas the cell reaction is reversible for NbSe₃, it is only partly reversible for TiS₃.
However, despite the alleged only partial reversibility of the TiS₃ cathode, it is
recommended, along with Nb and Ta chalcogenides, for Li non-aqueous batteries in a
patent [90]. Stressing the role of ternary phases in cathode behavior, Whittingham
considered five possible reactions between a Li anode and a TiS₂ cathode. The reaction
leading to the formation of Li$_x$TiS$_2$, where 0 < x < 1, seems the most probable, with better chance of reversibility [91].

Titanium dioxide received attention as a cathode material in non-aqueous batteries [92-94]. It exists in three crystal modifications such as rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic) [92]. Rutile and anatase both have a tetragonal structure with a disordered octahedral coordination of oxygen ions around the Ti$^{4+}$ cation, such that the number of edges shared by the octahedra increases from 2 (out of 12) in rutile to 4 in anatase. Although rutile has been assumed to be the most stable form because of its common occurrence, anatase is 8-12 kJ/mol more stable than rutile [93]. Titanium dioxide, in the anatase form, is an insertion host material which can accommodate lithium and exhibit reliably high lithium diffusivity. A striking difference in behavior between the two modifications of TiO$_2$, i.e. rutile and anatase, when used as cathodes in lithium primary cells was observed by Ohzuku and Kodama. [94]. Ohzuku showed that diffusion of lithium into the TiO$_2$ (anatase) was easier than for rutile, because of different structural features.

The electrochemical behavior of anatase TiO$_2$ has long been investigated as a positive electrode material for rechargeable non-aqueous lithium batteries [94]. The structure of anatase TiO$_2$ has the tetragonal space group of I4$_1$/amd with Ti$^{4+}$ ions (octahedral sites) at positions 4 (a) and O$^{2-}$ ions at positions 8 (e) [94]. The octahedral sites at the 4 (b) positions are vacant with respect to cations, and may accommodate cations having almost the same ionic radii as Ti$^{3+}$ (0.67 Å) and Ti$^{4+}$ (0.61 Å) as illustrated in fig. 2.10. The monovalent ions which may be accommodated at 4 (b) sites seem to be
Li$^+$ ions only (0.74 Å) because others are fairly large compared with Ti$^{3+}$ and Ti$^{4+}$, e.g. Na$^+$ (1.16 Å), K$^+$ (1.51 Å), Rb$^+$ (1.49 Å) and Cs$^+$ (1.70 Å).

Fig. 2.10 Structure of anatase TiO$_2$. Open circle, closed circle and x signs denote oxygen ions (8(e) sites) titanium ions (4(a) sites) and vacant octahedra (4(b) sites), respectively [94].
When electrons are inserted in Ti\textsuperscript{4+} ions (d\textsuperscript{0}) at positions 4(a), Ti\textsuperscript{3+} (d\textsuperscript{1}) are formed at the same positions. Electrons on Ti\textsuperscript{3+} ions may travel along 4(a) sites with the aid of thermal energy and an external electric field. Excess charge may be compensated by the accommodation of foreign ions (Li\textsuperscript{+} ions) at 4(b) sites in the anatase TiO\textsubscript{2} matrix. Li\textsuperscript{+} ions may also be mobile along 4(b) sites. Thus, the partially reduced anatase TiO\textsubscript{2} corresponds to the reduction process. The oxidation process is the reverse of this. Since the number of 4 (a) and 4 (b) sites are equal, a hypothetical topotactic reaction of anatase TiO\textsubscript{2} has been proposed to be [93] as follows

$$\square \quad \text{Ti}^{4+} \quad \text{O}^{2-} \quad + \quad \text{x Li}^{+} \quad + \quad \text{x e}^{-} \quad \overset{\text{Eq. [2.7]}}{\rightleftharpoons} \quad \text{Li}\textsubscript{x} \quad \text{Ti}^{4+}\textsubscript{1-x} \quad \text{Ti}^{3+}\textsubscript{x} \quad \text{O}^{2-}$$

\((4b) \quad (4a) \quad (8e) \quad \text{soln} \quad \text{(metal)} \quad (4b) \quad (4a) \quad (4a) \quad (8e)\)

\(\square\) denotes vacant sites.

The electrochemical behavior of TiO\textsubscript{2} in aqueous media is scantily reported in the literature.

### 2.2.3 Phospho-olivine type LiMPO\textsubscript{4} (M = Fe or Mn) as cathode material

Since the demonstration of reversible lithium intercalation between the layers of TiS\textsubscript{2} [91], considerable effort has been devoted to identification of other lithium-insertion compounds that can be used as cathode for a secondary non-aqueous battery, particularly lithium batteries [93].

The iron compounds containing polyanions such as SO\textsubscript{4}\textsuperscript{2-}, PO\textsubscript{4}\textsuperscript{3-}, AsO\textsubscript{4}\textsuperscript{3-} and even MoO\textsubscript{4}\textsuperscript{2-} or WO\textsubscript{4}\textsuperscript{2-} are known to lower the Fe\textsuperscript{3+/2+} redox energy levels which make them attractive for use in lithium batteries. Among the compounds which have a Nasicon
framework, for example Li₄Fe₂(SO₄)₃ [95], Li₃Fe₂(PO₄)₃ [96] and Li₂FeTi(PO₄)₃ [97], are potentially useful.

The open Nasicon framework allows fast Li⁺ ion diffusion, but a separation of the FeO₆ octahedra by polyanions reduces the electronic conductivity, which is polaronic in the mixed valence state. Hence, the cathode performance of an iron phosphate having an ordered olivine structure in which the FeO₆ octahedra share common corners has been investigated recently and proposed as a potential candidate as a cathode material in non-aqueous solvent/electrolyte batteries.

The ordered olivine structure with general formula LiMPO₄ have been extensively explored as a cathode material for non-aqueous systems [98]. These compounds contain tetrahedral “anion” structure units (XO₄)ⁿ⁻ with strong covalent bonding, generating oxygen octahedra occupied by other metal ions. Among the LiMPO₄ (M = Mn, Fe, Co and Ni), lithium iron phosphate (LiFePO₄) and lithium manganese phosphate (LiMnPO₄) have been recognized as promising cathode materials for lithium battery. This is mainly due to its low cost, environmental benignity, cyclic stability and a reversible capacity of over 125 mAh/g.

Olivine-type LiFePO₄ was first reported by Padhi et al [98] and subsequently, extensive work on LiFePO₄ has been carried out by a number of groups [99-102], particularly on the substitution of Fe with Mn, Co and Ni and their suitability as cathode materials. LiMnPO₄ and LiFePO₄ are the most attractive cathode materials owing to their high potential for use in batteries. Several problems with the use of LiFePO₄ as a cathode material have been reported [103]. The synthesis of LiFePO₄ is not easy because of the iron oxidation state, which is usually controlled by furnace heating with an inert gas flow.
for several hours [103-105]. Alternative synthetic processes reported recently [106-110] use divalent iron(II) compounds, typically iron(II) oxalate, FeC₂O₄·2H₂O, or iron(II) acetate, or Fe(OOCH)₂, as the starting material achieved success to synthesize LiFePO₄. Another significant drawback of LiFePO₄ is its low electronic conductivity, because this material is basically an electrical insulator [98]. The electronic conductivity of LiFePO₄ is (about 10⁻⁹ to 10⁻¹⁰ S/cm) [111] at ambient temperature which increases the impedance of the electrode and decreases the rate capability. This significantly limits its application in battery systems [103, 112-113] with considerable loss in utilization with increase in current, suggesting transport limitations. Because of this, it is found that the electrochemical extraction of lithium in LiFePO₄ is limited to about 0.6 Li atoms per formula unit [98]. Various solutions have been proposed and tested to alleviate this problem, with the most successful being adding carbon to improve the conductivity of the solid phase [104-105, 114]. The electronic conductivity of LiFePO₄ was enhanced by a factor ~ 10⁸ (10⁻² S/cm) [111] by the addition of carbon and the extraction of lithium in LiFePO₄ was about 1.0 Li atoms per formula unit. It is now a common practice to add conductive carbon powder in proportion anywhere from 5 % to 10 % by weight, to produce a cathode powder with sufficient conductivity for electrons. This carbon is added at the beginning of the synthesis where it is mixed into the material by solution method at a molecular size level [113].

LiMnPO₄ as a cathode material is quite attractive owing to the reasonable potential of the Mn³⁺/²⁺ redox couple. However, besides the original work of Padhi [98], only limited literature is available on LiMnPO₄ [115-116].
The crystal structure of LiMPO$_4$ with a crystallographic formula of M$_2$XO$_4$ has M atoms in half of the octahedral sites and X atoms in one-eighth of the tetrahedral sites of a hexagonal close packed (hcp) oxygen array. It is the hexagonal analogue of the cubic normal spinel X [M$_2$]O$_4$. Olivine crystallizes in preference to spinel for certain small X ions such as Be$^{2+}$, B$^{3+}$, Si$^{4+}$, P$^{5+}$, and occasionally Ge$^{4+}$. Unlike in the spinel (fig. 2.6), the two octahedral sites in olivine are crystallographically distinct and differ in size, which favors ordering in MM'XO$_4$ olivine's containing M and M' ions of different size and charge. The LiMPO$_4$ compounds, with M = Fe, Mn have the ordered olivine structure (fig. 2.11)

![Diagram of olivine crystal structure](image)

**Fig. 2.11** Olivine crystal structure [103]
Figure 2.11 shows the crystal structure of olivine: an ideal hcp model and the actual structure. In the actual structure, the M(1) site has I symmetry, the M(2) octahedron has mirror symmetry with average M-O distances greater than that in the M(1) octahedron. The M(1) sites form linear chains of edge-shared octahedra running parallel to the c-axis in the alternate a-c planes; the M(2) sites form zigzag planes of corner-shared octahedra running parallel to the c-axis in the other a-c planes. Each M(1) site shares its edges with two M(2) sites and two X sites; there is one edge-shared by an M(2) site with an X site [117]. Distortion of the hcp oxygen array has been related to the cation-cation coulomb repulsion across the shared edges. In the LiMPO₄ (M = Mn or Fe) compounds, the lithium occupy M(1) sites and the M atoms M(2) sites. With Li in the continuous chains of edge shared octahedra on alternate a-c planes, a reversible extraction/insertion of lithium from/into these chains would appear to be analogous to the two-dimensional extraction or insertion of lithium in the LiMO₂ layered oxides with M = Co or Ni. On the other hand, the XO₄ tetrahedra bridge between adjacent M(2) planes in the olivine structure, which constrains the free volume in which the Li⁺ ions move; only the Li-O bonding constrains the spacing between MO₂ layers in the LiMO₂ compounds.

The literature on phospho-olivine electrodes is limited only to non-aqueous media. Studies in aqueous media are scarcely reported.

2.3. References


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Chapter 3

Electrochemical behavior of Manganese dioxide as a cathode material in aqueous LiOH electrolyte

3.1 Introduction

As noted in chapter 2 the use of manganese dioxide as the positive active (cathode) material in Leclanché and alkaline manganese batteries is well known and characterized [1]. Primary cells (Leclanché and alkaline) are based on the electrochemical insertion of protons into the host lattice of MnO₂ [2]. Under certain conditions the insertion of protons in alkaline cells is reversible [2-3].

While intercalation of lithium ions into MnO₂ in non-aqueous electrochemical cells is well known, [4-7] there is very limited information on intercalation occurring in aqueous media [8]. This chapter describes an investigation of the electrochemical behavior of MnO₂ in aqueous LiOH. A particular objective has been to investigate what effect aqueous LiOH has when it is substituted for the traditional potassium hydroxide as the battery electrolyte in alkaline Zn-MnO₂ batteries. The aim was to determine the mechanism through which reduction/oxidation of MnO₂ occurs in LiOH as compared to that in KOH.

3.2 Experimental

Materials: EMD (γ-MnO₂) was purchased from the Foote mineral company. Zn foil (99.9%) from BDH chemicals; analytical reagent grade zinc sulphate heptahydrate (ZnSO₄·7H₂O) from Ajax Chemicals and lithium hydroxide monohydrate (LiOH·H₂O) from Sigma Chemicals were used in this study.
3.2.1 Galvanostatic discharge/charge of Zn/MnO$_2$-aq. LiOH Cells

The MnO$_2$ active material was first mixed with 15 wt.% of carbon black (A-99, Asbury USA) and with 10 wt.% of poly(vinylidene difluoride) (PVDF, Sigma Aldrich) as a binder and then pressed into a disc shape with a diameter of 12 mm. Each disk was 0.5 mm thick and weighed approximately 35 mg. An electrochemical test cell was constructed with the disk as the cathode, Zn metal as the anode and filter paper (Whatman filters 12) as the separator. A schematic diagram of the cell is shown in fig.3.1. The mass of zinc was at least tenfold in excess of that required for the stoichiometric reaction between Zn and MnO$_2$. The electrolyte was a saturated solution of lithium hydroxide containing 1 mol L$^{-1}$ zinc sulphate. Analytical reagent grade zinc sulphate heptahydrate (ZnSO$_4$·7H$_2$O), lithium hydroxide monohydrate (LiOH•H$_2$O) and potassium hydroxide (KOH) were dissolved in deionized water to prepare solutions of required concentrations.

The cells were charged/discharged galvanostatically at 0.5 mA/cm$^2$ by using an EG&G Princeton Applied Research Potentiostat/Galvanostat model 273A, operated by model 270 software (EG&G). The cutoff discharge and charge voltages were 1.0 and 1.9 V respectively. All electrochemical measurements were carried out at ambient temperature (25 ± 1°C).
Fig. 3.1 Schematic diagram of a Zn |MnO₂| aqueous LiOH cell.
3.2.2 Slow-scan cyclic voltammetric investigation of MnO₂

For cyclic voltammetric (CV) experiments, a standard three-electrode cell as shown in fig. 3.2 was used. For this purpose, the MnO₂ working electrode was made as follows: MnO₂ powder was pressed on to a disc of Pt gauze. On the other side of a disc, a layer of conductive carbon (A-99, Asbury USA) was also pressed. The MnO₂ side of the disc was exposed to the LiOH electrolyte through a Teflon barrel as shown in fig. 3.2. For making electrical connection of MnO₂ a Pt disc was inserted into the barrel on top of the carbon side which contacted a stainless steel plunger. The counter electrode was a zinc foil, which was separated from the main electrolyte by means of a porous frit. A saturated calomel electrode (SCE) served as the reference electrode. Reported
potentials are relative to SCE. The electrolyte was saturated aqueous lithium hydroxide. The working electrode was cycled between 0.4 and −0.7 V at 25 μV /s scan rate. On each occasion the potential scan started at 0.4 V, moving initially in the cathode direction.

3.2.3 Material characterization

For material characterization a Siemens X-ray diffractometer with Philips Co-Kα radiation is used. The surface analysis of the material was conducted by using a scanning electron microscope (Philips Analytical XL series 20). X-ray photoelectron spectroscopy (Kratos Ultra Axis Spectrometer) using monochromatic Al Kα (1486.6 eV) radiation was used to analyze the chemical binding energy of the samples. X-ray photoelectron spectrometry (XPS) analysis was started when the pressure in the analysis chamber fell below 1 x 10⁻⁹ hPa. Carbon, C (1s), was used as a reference for all the samples. The Fourier transform infrared spectrum (FTIR) was recorded using a Nicolet Magna-IR 850 spectrometer. For FTIR study, MnO₂ was mixed thoroughly with KBr and for each sample an average of 16 scans were recorded.

3.3 Results and Discussion

3.3.1 Galvanostatic discharge/charge characteristics of Zn/MnO₂-aqueous lithium hydroxide cell

There is substantial literature on the performance characteristics of MnO₂ in Zn-MnO₂ cells using aqueous potassium hydroxide as the electrolyte [2, 3, 9-11]. The use of highly conductive potassium hydroxide solution results in a lower internal resistance [9]. However the conductivity of the electrolyte is decreased by the dissolution of Zn(OH)₂ from the anode during the discharge cycle. Kordesch et al. [10] reported that the
discharge behavior of the cathode material, MnO$_2$, in the alkaline KOH electrolyte occurs in a heterogeneous phase reaction, i.e. MnO$_2$ being converted to Mn$_2$O$_3$. Hence, the MnO$_2$ lattice expands and, at a certain point of discharge, the mechanism changes to an irreversible portion of the MnO$_2$ reduction process. Donne et al. [3] have reported that the heterogeneous reduction of EMD to form Mn(OH)$_2$ was dependent on electrolyte concentration and EMD particle size. McBreen.[11] have studied the discharge processes that occur via heterogeneous reduction. All the related work is based on the electrochemical insertion of protons into EMD.

In accordance with the objectives of this project, the effect of replacing KOH with LiOH in Zn/MnO$_2$ cell was determined by carrying out discharge cycles on two identical cells, both containing 1 M ZnSO$_4$ but one containing aqueous saturated KOH and the

![Graph](image)

**Fig. 3.3** First discharge curve at 0.5 mA/cm$^2$ of Zn/MnO$_2$ cells using saturated aqueous of (a) KOH and (b) LiOH containing 1 mol L$^{-1}$ of ZnSO$_4$ under identical conditions.
other aqueous saturated LiOH. For easy comparison only one current density (0.5 mA/cm²) was used. The results for the first discharge cycle for both the cells are shown in figs. 3.3-3.5.

The discharge characteristics for the cell with KOH is quite different from that of the LiOH cell (fig. 3.3 a and b). The cathode material utilization as calculated from the initial weight of the active MnO₂ in the cathode for the KOH cell was 41 % (120 mAh/g) compared to 56 % (162 mAh/g) for the LiOH cell using a 1 V cutoff for both cells. The discharge capacity for LiOH, fig. 3.3 b, was higher and the decrease in cell potential was lower when LiOH was the electrolyte.

Figure 3.4 shows the reversibility of the cell Zn/MnO₂ with saturated aqueous LiOH containing 1 mol L⁻¹ of ZnSO₄ electrolyte. The cell could be reversibly discharged and charged. The shape of the discharge curve (in fig. 3.4) is characterized by an initial drop in voltage to 1.3 V, followed by a gradual downward-sloping potential profile until the 1 V cutoff voltage. The voltaic efficiency of 83% was obtained. The coulombic efficiency as a function of cycle number for various cycles is shown in fig. 3.5. The efficiency dropped rapidly during the first 5 cycles after which the decrease was gradual. At the 40th cycle the efficiency was only 16% suggesting that the material was degrading somewhat.
Fig. 3.4 The first discharge-charge profile of Zn/γ-MnO₂ cells using saturated aqueous LiOH containing 1 mol L⁻¹ of ZnSO₄ as the electrolyte.

Fig. 3.5 Coulombic efficiency vs. cycle number of Zn/γ-MnO₂ cells using saturated aqueous LiOH containing 1 mol L⁻¹ of ZnSO₄ as the electrolyte.
3.3.2 Physical characterization of the cathode material

In order to determine the mechanism by which the cathode material $\gamma$-MnO$_2$ discharged in the Zn/MnO$_2$ aqueous LiOH electrolyte cell, the discharged cathode material was characterized by XRD, SEM, XPS and IR.

3.3.2.1 X-ray diffraction studies

Figures 3.6 a and b show the x-ray diffraction patterns of the cathode material ($\gamma$-MnO$_2$) before and after discharge.

![X-ray diffraction patterns](image)

**Fig. 3.6** X-ray diffraction patterns changes of $\gamma$-MnO$_2$ after the electrochemical cycling in an aqueous battery: (a) $\gamma$-MnO$_2$ (before discharge), (b) upon discharge and (c) upon subsequent charge.

Because of the low crystallinity of the cathode material the x-ray diffraction pattern in fig. 3.6 a shows only broad Bragg reflections. As can be seen in fig. 3.6 b, an evolution of a new sharp peak at a d-spacing of 3.27 Å, and the corresponding shoulder at
a d-spacing of 3.18 Å is observed in the discharged γ-MnO₂ material. These peaks do not correspond to any of the MnOOH, Mn₂O₃ or Mn₃O₄ structures which are reported to be formed when aqueous KOH based Zn/MnO₂ cells are discharged [11]. This suggests that the discharge mechanism of this cathode material is not the same as that commonly reported for alkaline Zn-MnO₂ batteries. A close examination of the data suggests that the peaks correspond to those reported for non-aqueous lithium cells by Levi et al. [12]. The peaks corresponding to the d-spacing of 3.27 and 3.18 Å can be assigned to lithium-intercalated γ-β-MnO₂ (a hexagonal close-packed arrangement of oxygen, in which Mn and Li ions are located at octahedral sites), and the co-existence of two phases. The MnO₆-octahedral structure includes tunnels [1 x 1] and [1 x 2] in which Li ions should intercalate/de-intercalate during the discharge/charge process. Moreover, a comprehensive study of the intercalation mechanism by Ohzuku et al. [13] showed a similar diffraction peak at a d-spacing of 3.27Å for their heat-treated γ-MnO₂ during the discharge in a non-aqueous lithium cell; they ascribed it to γ-β-MnO₂. Figure 3.6 (c) also shows the x-ray diffraction pattern of the cathode material after recharging the discharged battery. A decrease in the intensity of the peak corresponding to γ-β-MnO₂ occurs. Hence, it can be inferred that the lithium intercalation is electrochemically reversible. However, it should be noted that the peak shifted to a lower angle. This is to be expected if the lithium ion was de-intercalated from the structure [14]. Balachandran and co-workers [15] have explained the differences resulting from the use of KOH and LiOH in terms of the relative ionic sizes of Li⁺ and K⁺ ions. As can be seen in fig. 3.7, the γ-MnO₂ is an inter growth of ramsdellite (R) and pyrolusite (P). The Mn(IV) O₆ octahedra of ramsdellite are linked into double chains, each of which consists of two adjacent single
chains that share octahedral edges [12, 15]. These double chains having tunnels with rectangular-shaped cross sections accept the A (A = Li⁺) cation, which is approximately the same size as that of Mn, the coulombic interactions dominate and hence the structure is stable for insertion/extraction of lithium ions. However, the size of the K⁺ ion is twice as that of Li⁺; therefore, the insertion site in fig. 3.7 is not stable as the electrostatic energy of the structure is diminished. Hence, unlike for Li⁺ the intercalation of K⁺ is not possible in γ-MnO₂.

![Diagram](image)

Fig. 3.7 Schematic diagram of (a) P: pyrolusite (b) R: ramsdellite and (c) γ-MnO₂, an intergrowth between ramsdellite (R), and pyrolusite (P), shown in the (001) plane [15].
3.3.2.2 SEM studies:

The SEM micrographs of the cathode material before and after discharge are shown in fig. 3.8. As can be seen from the micrograph, fig. 3.8 a, the particle size of the material before discharge was of the order of 20-25 μm. The material formed after the discharge had a very different morphology (fig. 3.8 b). The particle size was of the order 40-50 μm. It appears that during initial discharge the original γ-MnO₂ particles agglomerate into larger particles perhaps containing lithium ions intercalated into the material.

![SEM micrographs of γ-MnO₂ cathode material](image)

Fig. 3.8 Scanning electron micrographs of γ-MnO₂ cathode material (a) before discharge and (b) after discharge.

3.3.2.3 X-ray photoelectron spectroscopy (XPS) studies:

The cathodic material formed during the discharge cycle was further characterized by X-ray photoelectron spectrometry (XPS), a powerful tool for surface studies. A wide scan XPS spectrum of the surface (0-1400 eV) of this material is shown in fig. 3.9.
**Fig. 3.9** XPS spectrum (wide scan) of cathode manganese dioxide (γ-MnO₂) after electrochemical lithium intercalation.

The important feature to notice in fig. 3.9 is the highly dominant O (1s) peak, while the signals of other elements of interest are quite weak. The surface of the cathode material after discharge was covered with a thick overlayer of material deposited. This outer layer contained the elements C and O and Li. H cannot be detected with XPS. Consideration of the binding energies and relative concentrations suggests that this overlayer was composed of a mixture of LiOH, and Li₂CO₃. The presence of Li₂CO₃ could be explained in terms of the reaction of atmospheric CO₂ with the LiOH electrolyte when the cathode was taken out of the cell. Although it is not central to the objectives of this thesis the characteristics of the Li₂CO₃ over layer were investigated by XPS and SIMS techniques.
The outer layer required 5 hours of ion bombardment (4.0 kV, 2 μA, and 500μm spot) to remove it and reveal the underlying material. The thickness of this material was estimated to be 0.5 μm (assuming an etch rate of 1.7 nm per minute).

The XPS spectrum of the material after prolonged etching for 5 h (shown full scale, fig. 3.10) reveals the presence of the underlying elements Zn, Mn, and Li, with a much reduced intensity of O (1s). It is interesting to note that Zn was not seen on the undisturbed outer surface, but was present at the active surface of the MnO₂ material. This is clear evidence that the overlayer was porous with respect to ions. The ions could travel through the overlayer to the active MnO₂ material underneath.

**Fig. 3.10** XPS spectrum (wide scan) of the cathode manganese dioxide (γ-MnO₂) after electrochemical lithium intercalation upon argon ion etching for 5 hours.
Figure 3.11 shows the variation with concentration of the Li$_2$CO$_3$ and LiOH in the overlayer. Apparently the insoluble Li$_2$CO$_3$ forms a barrier to H$_2$O, but LiOH is able to move through the structure. The concentration of LiOH falls with depth into the solid in a profile that is not inconsistent with a diffusion driven process.

![Graph showing the variation of counts with etching time](image)

**Fig. 3.11** Variation in concentration of the Li$_2$CO$_3$ and LiOH upon depth profiling

In order to view the spectrum associated with each of the elements presented in fig. 3.9, the XPS spectra over regions specific to elements of interest were recorded over five sweeps. Figures 3.12-3.15 show the high resolution XPS spectra, as a function of argon ion etching of the material. It can be seen in fig. 3.12 that, after the first 30 min of bombardment, the O (1s) peak at 532 eV disappears. Instead two new peaks emerged -- one at 533 and the other at 530.1 eV. Furthermore, the peak intensity of the signal at 533 eV decreased with an increased argon ion etching period, whereas the intensity of the second signal peak at 530.1 eV remained fairly constant. Based upon binding energies as reported in the literature [16], the peaks were assigned at 533 eV to Li$_2$CO$_3$ and the second peak at 530.1 eV to MnO$_2$, present in the material itself.
Fig. 3.12 XPS spectra of O (1s) for the cathode manganese dioxide (γ-MnO₂) after electrochemical lithium intercalation, time in figure indicates the etching duration.

Fig. 3.13 XPS spectra of C (1s) for the cathode manganese dioxide (γ-MnO₂) after electrochemical lithium intercalation, time in figure indicates the etching duration.
Figure 3.13 shows the XPS spectra of C (1s) for the cathode material ($\gamma$-MnO$_2$) after discharge. Two types of carbon peaks were observed, one at 285 eV could be assigned to the hydrocarbons present in the electrode material, and the other at 291 eV could be assigned to carbon associated with Li$_2$CO$_3$. The peak at 285.0 eV, which had a very weak signal before argon ion bombardment, increased in intensity on continuous etching of the overlayer. The other peak at 291 eV in fig. 3.13 corresponding to Li$_2$CO$_3$ is formed and then removed after etching indicating that insoluble Li$_2$CO$_3$ forms a barrier to H$_2$O. This is consistent with the change in the O (1s) as discussed above for fig. 3.12.

Figure 3.14 focuses on the region where Li (1s) and Mn (3s) are expected to occur. It can be seen that the peak at 55.6 eV, which was assigned to the presence of

![XPS spectra](image)

**Fig. 3.14** XPS spectra of Li (1s) and Mn (3s) for the cathode manganese dioxide ($\gamma$-MnO$_2$) after electrochemical lithium intercalation, time in figure indicates the etching duration.
Li$_2$CO$_3$ in the unetched material, decreased in intensity on etching. The prolonged etching showed the emergence of another peak at 56.3 eV. This peak is assigned to the underlying lithium intercalated within manganese dioxide, Li$_x$MnO$_2$ [12]. The basis of this assignment is that the Li species is such that the binding energy of the 1s electron is greater than that of Li in Li$_2$CO$_3$. This is likely to be the case with the Li$^+$ ion intercalated into the highly oxidizing environment of the MnO$_2$ structure. The signal at 48 eV, which was barely visible in the unetched material, increased in intensity as the etching period increased. This signal is quite pronounced after 3 hrs of etching and clearly indicates the presence of Mn, as seen in fig. 3.14.

Figure 3.15 shows the XPS spectra of Mn (2p). As was observed for the Mn (3s)

![Image of XPS spectra](image_url)

**Fig. 3.15** XPS spectra of Mn (2P) for the cathode manganese dioxide ($\gamma$-MnO$_2$) after electrochemical lithium intercalation, time in figure indicates the etching duration.
signal, prolonged argon gas etching (3 h) also resulted in increased intensity of the Mn 2p_{1/2} and 3p spin orbit split components. Thus, removal of the outer layer by argon ion etching assists in exposing the true discharge products of the cathode material in saturated LiOH electrolyte. From the evidence based on the XRD and XPS studies, it can be concluded that lithium is indeed intercalated electrochemically into the host framework of γ-MnO_2 when aqueous LiOH is the electrolyte.

3.3.2.4 Infra-red (IR) spectral studies:

The IR spectra of γ-MnO_2, before and after discharge are shown in fig. 3.16. The material before discharged had only one peak [17] at 607 cm\(^{-1}\). The discharged material showed strong broad bands at 1470 - 1520 cm\(^{-1}\) and a sharp peak at 875 cm\(^{-1}\). These could be assigned to lithium carbonate (Li_2CO_3) [18]. As noted earlier Li_2CO_3 is formed

![Fig. 3.16 FTIR spectra of the γ-MnO_2 cathode before and after the first discharge cycle in Zn/MnO_2-LiOH aqueous battery. Peak labels A - main octahedral vibration and B, C - C-O in Li_2CO_3.](image-url)
by reaction of the LiOH electrolyte with atmospheric CO₂. The spectrum also has two strong absorption peaks “A” and “B” at 607 and 875 cm⁻¹ respectively and a strong band “C” at 1470-1520 cm⁻¹. The peaks below 800 cm⁻¹ (fig. 3.17) are assigned to fundamental

Fig. 3.17 FTIR spectra of γ-MnO₂ cathode (a) before discharge (b) after discharge, and (c) chemically substituted LiMnO₂.
vibrations of MnO$_6$ octahedra [18]. The important thing to note here is that on discharge
the material had an additional peak at 550 cm$^{-1}$. This new peak is assigned to the Li-
intercalated MnO$_2$ in which the Mn is in the Mn(III) oxidation state. This assignment is
confirmed by preparing a sample of lithium-intercalated MnO$_2$ by the method described
by K. Ishibashi [19] and recording its IR spectra under identical conditions. This is shown
in fig. 3.17 c. The two spectra 3.17 b and 3.17 c are similar. Both show two peaks (A and
A$_1$ in figs. 3.17 b and 3.17 c) in the region 500-650 cm$^{-1}$. This confirms that the product
of discharge of $\gamma$-MnO$_2$ is indeed lithium-intercalated MnO$_2$.

3.3.3 Slow scan cyclic voltammetric investigation of MnO$_2$

This section describes the results of the study focused on the mechanism of the
intercalation of lithium. The study involved slow scan voltammetry together with
characterization of the materials that are formed during the electrochemical discharge of
$\gamma$-MnO$_2$ by techniques like X-ray diffraction (XRD) and scanning electron microscopy
(SEM).

Figure 3.18 shows the first cyclic voltammogram (CV) of $\gamma$-MnO$_2$ under the
conditions noted in the figure. As can be seen in fig. 3.18, the CV profile consists of a
reduction peak C$_1$ at $-480$ mV and a corresponding anodic peak A$_1$ at $-160$ mV. A small
shoulder at 46 mV is also seen during the scan in the anodic direction.
**Fig. 3.18** Cyclic voltammogram of MnO$_2$ in LiOH for the first cycle, potential scanned at 25 µV. s$^{-1}$ from +0.4 to −0.6 V and back.

Figure 3.19 shows the changes in the CV profile when the material is subjected to continuous cycling (20 cycles) in the potential region +0.4 to −0.6 V. The cathodic and anodic peak currents decreased slightly up to about ten cycles and then tended to stabilize suggesting that the material could be reversibly reduced/oxidized over a number of cycles. The ratio of the charge under the peaks $C_1$ and $A_1$ was 0.81 suggesting that the reaction was 81% reversible. To confirm that the anodic peak corresponded to the reduction reaction at −480 mV, the following experiment was done. The $\gamma$-MnO$_2$ was scanned cathodically up to −480 mV and then held constant at that point for 0, 20 and 40 min.
Fig. 3.19 Cyclic voltammogram of MnO$_2$ in LiOH for the repeated cycles, potential scanned at 25 µV. s$^{-1}$ from +0.4 to −0.6 V and back.

At the end of the holding potential, the scan was reversed and the anodic peak current measured. The data are shown in fig. 3.20.

As can be seen from fig. 3.20 the anodic peak current increases as the time for which the electrode is held constant at potential − 480 mV increases. The material formed in the above experiment was characterized by X-ray diffraction. The results are shown in fig 3.21. This figure shows very few Bragg reflections indicating a low crystallinity of the material. The cathodic reduction of this material gave rise to two distinctly sharp diffraction peaks at d-spacings of 5.28 and 3.38 Å for a holding time to 20 min. Doubling the potential holding time to 40 min resulted in decrease in the intensity of the peak at 5.28 Å but increase in the peak at 3.38 Å. The peak at 5.28 Å is assigned to lithium-intercalated γ-MnO$_2$ and that at 3.38 Å to lithium-intercalated γ-β-MnO$_2$ based on the reported values in the literature [12]. The lithium-intercalated γ-β phase dominates when
the potential is held at – 480 mV over longer periods. This observation confirms that the 
electroreduction of $\gamma$-MnO$_2$ was reversible.

**Fig. 3.20** Cyclic voltammogram of MnO$_2$ in LiOH, potential held at – 480 mV. Time in 
figure indicates the (holding time) lithium concentration.

**Fig. 3.21** X-ray diffraction pattern of the material formed when the $\gamma$-MnO$_2$ is held at – 
480 mV Vs. SCE for various periods (a) 0 (b) 20 and (c) 40 min.
The behavior of MnO$_2$ in aqueous LiOH can be compared to that in aqueous KOH by referring to fig. 3.22. The data for both the electrolytes were obtained under identical conditions. The CV’s of MnO$_2$ in the two electrolytes are quite different. While the reduction peak in KOH occurs at −584 mV, the cathodic peak in the presence of LiOH is at −480 mV. Based upon what is known in literature, for KOH electrolyte the cathodic peak could be assigned to the formation of Mn(OH)$_2$ [11, 20] and the corresponding anodic peak at −138 mV to the oxidation of Mn(OH)$_2$ to a variety of Mn$^{3+}$ intermediates, including γ-Mn$_2$O$_3$, γ-MnOOH and β-MnOOH [11, 20-21]. For LiOH electrolyte the peak at −480 mV corresponds to the formation of a lithium-intercalated Li$_x$MnO$_2$ phase as discussed earlier and the corresponding anodic peak is reverse of this reaction.

Fig. 3.22 Cyclic voltammogram of γ-MnO$_2$ in LiOH and KOH electrolytes. The potential scanned at 25 µV. s$^{-1}$ from +0.4 to −0.6 V and back.
3.3.3.1 SEM studies

The surface morphologies of the materials formed during reduction and oxidation of \(\gamma\)-MnO\(_2\) in LiOH and KOH electrolytes were determined by scanning electron microscopy. The SEM micrograph of the \(\gamma\)-MnO\(_2\) before subjecting to reduction/oxidation is shown in fig. 3.23.

![SEM micrograph of \(\gamma\)-MnO\(_2\) cathode](image)

**Fig. 3.23** SEM micrograph of the \(\gamma\)-MnO\(_2\) cathode (as-received)

As can be seen from this micrograph (fig. 3.23), the material before electroreduction was crystalline with particle size varying from 20-100 \(\mu\)m. Some of the particle might have been agglomerised. Although the x-ray diffraction pattern of this material showed an amorphous hump which could be due to its low crystallinity, the microstructure appears to be crystalline. The new phase (\(Li_x\)MnO\(_2\)), which was formed on repeated cycling, fig. 3.24 a, had a much finer particle size (5-7 \(\mu\)m) compared to the un-cycled material.
Fig. 3.24 SEM images of the cycled $\gamma$-MnO$_2$ cathode (a) after reduction at $-480$ mV and (b) after subsequent re-oxidation via cyclic voltammetry in LiOH media.

The subsequent oxidation of the reduced material produced a phase (fig. 3.24 b) whose characteristics were quite similar to those of the original $\gamma$-MnO$_2$ (fig. 3.23). The
particle size was 15-20 μm. Thus the reduction/oxidation was reversible. This contrasts with the material formed after reduction/oxidation cycle of γ-MnO₂ in KOH (fig. 3.25 a and b). In KOH the γ-MnO₂ underwent an irreversible change during the cycle.

![SEM images](image)

**Fig. 3.25** SEM images of the cycled γ-MnO₂ cathode (a) after reduction at −584 mV and (b) and at subsequent re-oxidation via cyclic voltammetry in KOH media.
3.4 Conclusions

The charge-discharge cycle (battery) of zinc/\(\gamma\)-manganese dioxide alkaline cell containing aqueous LiOH electrolyte show that the cell with aqueous LiOH electrolyte functions quite differently from the traditional cell, which uses aqueous KOH. When a cell containing aqueous LiOH is discharged, lithium is intercalated into the host framework structure of the positive electrode material, manganese dioxide (\(\gamma\)-MnO\(_2\)). The formation of this material is confirmed through XRD and XPS studies of the positive electrode material before and after discharge and upon subsequent charge/discharge cycling. The mechanism of discharge of \(\gamma\)-MnO\(_2\) differs from the usual production of MnOOH, Mn\(_2\)O\(_3\) or Mn\(_3\)O\(_4\), which occurs when KOH is the electrolyte. The LiOH-based cell can be reversibly discharged and charged. Under the investigated conditions, 56% (162 mAh/g) of the theoretical capacity of the positive electrode active material (\(\gamma\)-MnO\(_2\)) to 1 V cutoff voltage could be achieved. The voltaic efficiency at the first cycle was found to be 83% when the battery was charged and discharged galvanostatically at 0.5 mA/cm\(^2\) current density.

Cyclic voltammetry coupled with X-ray diffraction (XRD) and scanning electron microscopy (SEM) show that the reduction of \(\gamma\)-MnO\(_2\) in LiOH produces a new phase of lithium ion intercalated MnO\(_2\) and is reversible. The differences in the mechanisms through which \(\gamma\)-MnO\(_2\) undergoes electroreduction/oxidation in aqueous LiOH and aqueous KOH can occur be explained in terms of relative ionic sizes of Li\(^+\) and K\(^+\) ions. Li\(^+\) ions, being comparable in size to Mn\(^{4+}\), are intercalated into the octahedral structure of \(\gamma\)-MnO\(_2\) while that is not possible for the larger K\(^+\) ion.
3.5 References


Chapter 4

Comparison of the behavior of electrolytic manganese dioxide and chemically prepared battery-grade MnO₂ in Zn|MnO₂|aqueous LiOH electrolyte

4.1 Introduction

4.1.1 Alkaline manganese dioxide batteries

As noted earlier in chapter 2, alkaline manganese dioxide battery uses manganese dioxide as cathode, an aqueous KOH electrolyte and zinc metal as anode. Commercial alkaline cells use electrolytic manganese dioxide [1-10] (EMD, a form of γ-MnO₂ – Section 3.1) rather than chemical MnO₂ or natural ore because of its higher manganese content, and its greater purity. Zinc is used as the anode material because of its good electrochemical behavior, compatibility with the battery electrolyte, reasonably good shelf life and low cost. The battery reaction involves anodic oxidation of Zn to Zn(OH)₂, and cathodic reduction of MnO₂ to MnOOH. Formation of Mn₃O₄ is also possible under slow discharge [11-14]. The total cell reaction on continuous discharge for one electron per mole of MnO₂ can be formally written as:

\[ 2 \text{MnO}_2 + \text{Zn} + 2\text{H}_2\text{O} \rightarrow 2 \text{MnOOH} + \text{Zn(OH)}_2 \]  \hspace{1cm} [Eq. 4.1]

In Chapter 3, the mechanism for electrochemical reduction/oxidation of EMD was shown to occur differently in LiOH electrolyte from that in the traditional aqueous KOH
electrolyte. As described earlier (Chapter 3), the reduction of MnO₂ in the presence of aqueous LiOH occurs via a Li⁺ intercalation mechanism. The focus of this chapter is on comparing the behavior of electrolytic manganese dioxide (EMD) and chemically prepared battery-grade MnO₂ (BGM) in LiOH electrolyte.

4.2 Experimental

The EMD and BGM used in this work were purchased from the Foote Mineral Company and Sigma Aldrich respectively. The theoretical maximum deliverable electrochemical capacity per unit weight for a one-electron process for both the materials is calculated to be 289 mAh/g.

The cell design and experimental details were similar to those noted in Chapter 3. For X-ray analysis a Siemens X-ray diffractometer using Philips Co-Kα radiation was used. The FTIR spectrum was recorded by using a Nicolet Magna-IR 850 spectrometer. The EMD and BGM were mixed thoroughly with KBr (spectroscopic grade). The mixtures were examined by transmission mode FTIR spectroscopy. For each sample an average of 16 scans were recorded. The surface analysis of the materials was conducted by using a scanning electron microscope (Philips Analytical XL series 20). Thermogravimetric analysis (TG) of the sample was conducted by using a TA Instruments (SDT 2960). A Kratos Ultra Axis Spectrometer using monochromatic Al Ka (1486.6 eV) radiation was used to analyze the chemical binding energy of the samples. The XPS analysis was carried out at pressures below 1 x 10⁻⁷ Pa.
4.3 Results and Discussion

4.3.1 Characterization of the MnO₂ materials

The EMD and the BGM were characterized by X-ray diffraction (XRD), infra-red (IR) spectra, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). Figures 4.1 a and b show the differences in the X-ray diffraction patterns of the two MnO₂ materials. The XRD peaks of EMD are broad and poorly defined. This is ascribed to non-periodic intergrowth of pyrolusite and ramsdellite structural units [10]. The XRD pattern of the battery-grade manganese dioxide material (fig. 4.1 b), contained four diffraction peaks with 2θ angles 16.3°, 19.7°, 29.7° and 31°. Different researchers have reported different 2θ values for this material, which is explained in terms of variation of composition of the constituent ramsdellite and pyrolusite phases [15-17]. The diffraction peaks at the 2θ angle of 29.7° can be assigned to presence of OH bonds in

![X-ray diffraction patterns](image)

Fig. 4.1 X-ray diffraction patterns of (a) EMD and (b) BGM before discharge.
the structure and the peak at 31° to β-MnO₂. The remaining peaks at 16.3° and 19.7° are characteristic of the γ-phase MnO₂ [16].

The FTIR spectra of the EMD and BGM are compared in fig. 4.2. The spectral features of both are almost identical indicating the presence of similar phases. The region below 1400 cm⁻¹ contains peaks due to fundamental vibrations of MnO₆ octahedra and the region above 1400 cm⁻¹ contains peaks primarily corresponding to OH vibrations. The absorption band at 3183 cm⁻¹, which is predominant for the battery-grade material (fig. 4.2 b) corresponds to structural or chemically bonded water [18]. This water is lost on heating as can be seen from fig. 4.3.

Fig. 4.2 FTIR spectra of (a) EMD and (b) BGM. A: main MnO₂ octahedral vibration and B: bonded OH.
Fig. 4.3 Thermogravimetric analysis of (a) EMD and (b) BGM

No such loss occurs for the EMD material. Figure 4.3 also shows that there is a change in phase of the BGM when heated to around 500°C. Thus, while the EMD retains its phase structure on heating the BGM does undergo a phase transformation. This probably relates to the change of γ-phase to β-phase. SEM characterization indicates that the EMD and the battery-grade MnO₂ have quite different morphologies. The SEM results in fig. 4.4 a and b indicate show that the battery grade material was less crystalline with finer particle size as compared to the EMD material.
4.3.2 Electrochemical characterization of Zn/MnO₂-aqueous LiOH cell

Figure 4.5 shows the difference in the discharge characteristics of Zn/MnO₂-aqueous LiOH cells containing EMD and BGM as cathode materials. The open-circuit voltage (OCV) of the cell with BGM is higher and the cell discharged at a higher voltage under identical conditions. The voltaic efficiency for the battery with BGM was 86 % as compared to 83 % for EMD at the first cycle at 0.5 mA/cm².
Fig. 4.5 Voltage versus discharge capacity of Zn/ MnO$_2$- LiOH (sat.) containing 1 M ZnSO$_4$ cells (a) EMD and (b) BGM.

However, the active material utilization of the BGM was lower than that for the EMD material under identical mass composition. This is probably related to the difference in the composition of the two MnO$_2$ materials with respect to ramsdellite and pyrolusite, water content and surface area. The two MnO$_2$ materials exhibited quite different rechargeability when subjected to continuous discharge/charge cycles. For example, while a 35% drop in the active material utilization occurred at cycle number 2 for the cell containing BGM, the same drop occurred at the 20$^{th}$ cycle for EMD. Thus the EMD was more stable to discharge/charge cycling.
4.3.3 Physical characterization of the products formed on discharge of MnO₂ in Zn/MnO₂-aqueous LiOH cells

The materials that were produced on discharge of EMD and BGM in Zn/MnO₂-aqueous LiOH batteries were characterized by X-ray diffraction. As noted earlier the XRD patterns of the two starting MnO₂ materials were quite different (fig. 4.1). However the two materials on discharge (fig. 4.6) had almost identical XRD patterns. For the EMD material d-spacing of 3.27 Å (2θ =31.7°) is ascribed to the formation of Li-intercalated MnO₂ phase (Li,MnO₂) [19]. For the BGM, d-spacing of the peak was at 3.32 Å (2θ = 31.2°). This difference is to be expected because the two phases could differ in the amount of intercalated-lithium.

![X-ray diffraction patterns](image)

**Fig. 4.6** X-ray diffraction patterns of (a) EMD and (b) BGM after discharge.
The XPS spectra of Li (1s) of the two discharged materials (EMD and BGM) are shown in fig. 4.7. The peaks are assigned with reference to the values reported in the literature [20-21]. Both the discharged materials show Li (1s) peaks at 54.4 eV, which is attributed to lithium intercalated manganese dioxide (Li$_x$MnO$_2$) suggesting that both the materials produced the same product on discharge in the presence of LiOH.

![XPS spectra of Li (1s) for the discharged materials](image)

**Fig. 4.7** XPS spectra of Li (1s) for the discharged (a) EMD and (b) BGM.

### 4.4 Conclusions

The physical characteristics of electrolytic manganese dioxide (EMD) used in this work were quite different from those of the chemically prepared battery grade manganese dioxide (BGM). The XRD patterns of the two materials show that BGM was less crystalline and smaller in particle size compared to EMD. The cathodic behavior of the two materials in Zn/MnO$_2$-aqueous lithium hydroxide differs significantly. The cells with BGM have higher OCV than those with EMD. The BGM cell discharges at a higher
voltage when discharged at the same current density, 0.5 mA/cm². Thus the voltaic
efficiency of the cell with BGM is higher than that with EMD. Even though the phase
composition of the two starting materials is different, on discharge in aqueous LiOH
electrolyte, both produce the same product which is assigned to be lithium intercalated
manganese dioxide. EMD is more stable to discharge/charge cycling than BGM.

4.5 References

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Chapter 5

Electrochemical behavior of anatase TiO₂ in aqueous LiOH electrolyte

5.1 Introduction

A brief review of TiO₂ including its physical characteristics and electrochemical properties when used as a cathode material in non-aqueous electrolytes is given in Chapter 2. As is noted in that chapter there is very little information in the literature on the electrochemical behavior of TiO₂ in aqueous media. Lyon and Hupp [1-2] reported that the electrochemical reduction of TiO₂ involves irreversible proton uptake (protonation) in aqueous H₂SO₄ or NaOH electrolytes. This mechanism was supported by electrochemical quartz crystal microbalance (EQCM) measurements. TiO₂ (anatase) has been extensively studied in non-aqueous media. In view of the main objective of this thesis, this chapter reports an investigation of the electroreduction/oxidation behavior of TiO₂ (anatase) in aqueous lithium hydroxide media in order to compare the results with those reported in non-aqueous lithium ion electrolytes [3-10]. The focus is on establishing whether the mechanism for the redox reaction of TiO₂ as a cathode material in aqueous LiOH electrolyte is similar or different from its behavior in non-aqueous Li⁺ electrolytes.

5.2 Experimental

The following chemicals were used in this study: TiO₂ (99.9%) obtained from Aldrich Chemical Company, Zn foil (99.9%) from BDH chemicals; analytical reagent
grade zinc sulphate heptahydrate (ZnSO₄·7H₂O) from Ajax Chemicals and lithium hydroxide monohydrate (LiOH·H₂O) from Sigma Chemicals.

The TiO₂ was mixed with 15 wt% of carbon black and 10 wt% of PVDF as a binder and pressed into a disk of 12 mm diameter. Each disk was 0.5 mm thick and weighed approximately 30 mg. An electrochemical test cell was constructed with the disk as the cathode, Zn metal as the anode with a filter paper (Whatman filters 12) as a separator between the anode and the cathode. The mass of zinc was at least 10-fold in excess of that required for the stoichiometric reaction between Zn and TiO₂. A saturated solution of lithium hydroxide containing 1 mol L⁻¹ zinc sulphate was used as the electrolyte.

The TiO₂| aqueous LiOH, ZnSO₄| Zn cells were discharged galvanostatically at 0.25 mA/cm² by using an EG&G Princeton Applied Research Potentiostat/Galvanostat model 273A, operated by model 270 software (EG&G). The cutoff discharge voltage was 0 V. All electrochemical measurements were carried out at room temperature (25 ±1°C).

For the cyclic voltammetric studies the standard three-electrode system as described in section 3.2 was used. The cathode consisted of TiO₂ mixed with 20 wt% conductive carbon (A-99, Asbury USA) pressed on to a 1.2 cm² disc of Pt gauze. The electric contact was made through the Pt gauze. The counter electrode was a zinc foil, which was separated from the main electrolyte by means of a porous frit. A saturated calomel electrode (SCE) served as the reference electrode. The electrolyte was a saturated solution of lithium hydroxide. The working electrode was cycled between 0 and
–0.7 V each time starting at 0 V and going initially in the cathodic direction at 25 µV/s scan rate in all experiments.

The products formed during discharge and charge cycles were characterized by a Siemens X-ray diffractometer using Philips Co Kα radiation. X-ray photoelectron spectroscopy (Kratos Ultra Axis Spectrometer) using monochromatic Al Kα (1486.6 eV) radiation was used to analyze the chemical binding energy of the samples. The XPS analysis was started when the pressure in the analysis chamber fell below 1 x 10⁻⁹ h Pa. The Fourier transform infrared (FTIR) spectrum was recorded by using a Nicolet Magna-IR 850 spectrometer. For the FTIR study, TiO₂ was mixed thoroughly with KBr and for each sample an average of 16 scans was recorded.

5. 3 Results and Discussion

5.3.1 Electrochemical behavior of Zn/TiO₂ – aqueous LiOH cell

A typical discharge curve of the Zn/TiO₂ aqueous LiOH cell is shown in fig. 5.1. The initial open circuit voltage (OCV) was 0.9 V. On discharge at a current density of 0.25 mA/cm², the cell voltage dropped rapidly to about 0.2 V and then gradually decreased. Even though the discharge voltage is very low, some information on material utilization could still be derived. As can be seen from Fig. 5.1, the percentage of material utilization was very low.
Fig. 5.1 The first discharge profile of Zn/TiO$_2$ cells using saturated aqueous LiOH containing 1 mol L$^{-1}$ of ZnSO$_4$ as the electrolyte at 0.25 mA/cm$^2$.

5.3.1.1 Cyclic Voltammetric behavior of TiO$_2$

Figure 5.2 shows a typical cyclic voltammogram (CV) of anatase TiO$_2$ used in this study. During the first cathodic sweep, two peaks C$_1$ and C$_2$, at potentials $-396$ mV and $-496$ mV respectively are seen. During the reverse anodic sweep only one peak A$_1$ at $-200$ mV, was observed. On repeated cycling, the peaks became more defined (fig. 5.3). At the fifth cycle, the reduction peak C$_1$ at $-396$ mV almost disappeared and the peak at $-496$ mV became more pronounced.
**Fig. 5.1** The first discharge profile of Zn/TiO$_2$ cells using saturated aqueous LiOH containing 1 mol L$^{-1}$ of ZnSO$_4$ as the electrolyte at 0.25 mA/cm$^2$.

**5.3.1.1 Cyclic Voltammetric behavior of TiO$_2$**

Figure 5.2 shows a typical cyclic voltammogram (CV) of anatase TiO$_2$ used in this study. During the first cathodic sweep, two peaks $C_1$ and $C_2$, at potentials $-396$ mV and $-496$ mV respectively are seen. During the reverse anodic sweep only one peak $A_1$ at $-200$ mV, was observed. On repeated cycling, the peaks became more defined (fig. 5.3). At the fifth cycle, the reduction peak $C_1$ at $-396$ mV almost disappeared and the peak at $-496$ mV became more pronounced.
**Fig. 5.2** Cyclic voltammogram of TiO$_2$ (first cycle) (scan rate: 25μv.s$^{-1}$; potential limit: 0 to −0.6 V and back).

**Fig. 5.3** Effect of repeated voltammetric cycling on the current vs. potential profile of TiO$_2$ in aqueous LiOH (scan rate: 25μv.s$^{-1}$; potential limit: 0 to −0.65 V and back). The numbers in figures denote cycle number.
**Fig. 5.4** Effect of holding potential at $-496$ mV for various intervals on the current-voltage profile of TiO$_2$ in aqueous LiOH (scan rate: $25\mu$V.s$^{-1}$; potential limit: 0 to $-0.65$ V and back).

Correspondingly, the oxidation peak at $-200$ mV became narrow. These observations suggest that during the first cycle two reduction processes occur, but only one corresponding oxidation process occurs during the reverse scan.

To establish whether the anodic peak at $-200$ mV corresponded to the reduction reaction occurring at $-496$ mV (peak C$_2$), the following experiment was performed. The TiO$_2$ was scanned cathodically to $-496$ mV where the potential was then held constant for 30, 60 and 90 min. At the end of these periods, the scan was reversed. The results are shown in fig. 5.4. Only one anodic peak at -200 mV was seen and the anodic peak current increased, as the time for which the electrode potential was held constantly increased.

The product of electroreduction of TiO$_2$ was identified by various techniques as described in the following sections.
5.3.2 Physical Characterization of TiO$_2$ and the products formed during cell charge/discharge and cyclic voltammetric investigations

5.3.2.1 X-ray diffraction studies

The X-ray diffraction pattern of the TiO$_2$ used in this study is shown in fig. 5.5. This matches that of anatase TiO$_2$ (JCPDS pattern 21-1272) and all diffraction lines were indexed in terms of $(h k l)$ having a tetragonal lattice with $a = 3.792$ Å and $c = 9.514$ Å.

![X-ray diffraction pattern of Anatase TiO$_2$](image)

**Fig. 5.5** X-ray diffraction pattern of Anatase TiO$_2$

Figure 5.6 shows the X-ray diffraction pattern of the material formed on scanning TiO$_2$ to $-496$ mV, the potential where reduction occurs. After the first cycle reduction,
Fig. 5.6 X-ray diffraction patterns of titanium dioxide (TiO$_2$) before and after electoreduction at -496 mV: (a) before reduction; (b) at first reduction; (c) after subsequent oxidation; (d) at third reduction; (e) at fifth reduction.
the X-ray diffraction pattern is almost identical to that in fig. 5.6 a except that two new peaks at $2\theta = 47.0^\circ$ and $54.7^\circ$ are seen (fig. 5.6 b). The peaks at $2\theta = 47.0^\circ$ and $54.7^\circ$ are assigned to Ti$_2$O and TiO respectively. The subsequent oxidation of the material formed in the first reduction cycle regenerates the original material. The XRD pattern of the regenerated material is almost identical to that of the original unreduced TiO$_2$ except that the peaks are shifted slightly to higher $2\theta$ values (fig. 5.6 c). The sample after the third reduction did not have the peaks corresponding to $2\theta = 47.0^\circ$ and $54.7^\circ$ but had three new peaks at $2\theta = 37.3^\circ$, $44.9^\circ$ and $52.3^\circ$, fig. 5.6 d. The peak at $2\theta = 37.3^\circ$ is assigned to Ti$_2$O$_3$ and those at $44.9^\circ$ and $52.3^\circ$ are assigned to Li$_x$TiO$_2$ [10-11]. The material after the fifth reduction scan had highly developed four peaks at $2\theta = 41.2^\circ$, $43.8^\circ$, $44.9^\circ$ and $52.3^\circ$ (fig. 5.6 e). All these peaks are assigned to Li$_x$TiO$_2$ [10-11]. This indicates that the electroreduction of TiO$_2$ leads to the formation of intercalated TiO$_2$ together with some Ti$_2$O$_3$. Since the ionic radius of Li$^+$ is almost identical to that of Ti$^{3+}$ (~ 0.7 Å) the formation of lithium-intercalated TiO$_2$ is not surprising. In this regard, the behavior of TiO$_2$ in aqueous LiOH electrolyte is similar to that in non-aqueous LiClO$_4$ electrolyte. The formation of Li$_x$TiO$_2$ in the non-aqueous media is well known [10, 12-15].

At this stage it is not possible to conclusively identify the peaks at $2\theta = 47.0^\circ$ and $54.7^\circ$ which were seen only during the first cycle. This could be postulated to arise from some trace impurity in the sample.

**5.3.2.2 X-ray photoelectron spectroscopy studies**

Figure 5.7a shows the X-ray photoelectron spectra (XPS) of the TiO$_2$ before reduction – 496 mV. The symmetric Ti (2p) peaks indicate the material to be
stoichiometric TiO$_2$ with a low concentration of defects. The spin-orbit splitting was 5.6 eV, with an intensity ratio of 0.26 between Ti (2p$_{1/2}$) and Ti (2p$_{3/2}$). Figure 5.7 b shows Ti (2p) peaks of the same material after electroreduction at the fifth scan. As can be seen in fig. 5.7b, a clear chemical shift of Ti (2p) towards lower binding energy is observed. This chemical shift reflects the change of Ti$^{4+}$ to Ti$^{3+}$ oxidation state. Ebina et al and Sodergren et al [14, 16] also observed a similar chemical shift of Ti (2p) when TiO$_2$ was electroreduced in non-aqueous LiClO$_4$ electrolyte, indicating the formation of a lithium-intercalated TiO$_2$ phase (Li$_x$TiO$_2$).

![Graph](image)

**Fig. 5.7** XPS spectra of Ti 2p (3/2) and (½) of titanium dioxide (TiO$_2$): (a) before; (b) after electroreduction at −496 mV.

Figure 5.8 shows the XPS spectra of the Li (1s) region of TiO$_2$ before and after electroreduction. For the unreduced sample no signal corresponding to Li (1s) is seen (fig. 5.8 a), instead, only a small peak of Ti (3s) at 59.5 eV region occurs.
Fig. 5.8 XPS spectra of Ti (3s) and Li (1s) of titanium dioxide (TiO₂): (a) before; (b) after electroreduction at −496 mV.

The material after reduction (fig. 5.8 b) contained a highly developed peak corresponding to Li (1s) [17] at 55.1 eV. To eliminate the possibility that the observed Li (1s) signal for the electroreduced sample was not just due to some lithium ion impurity such as Li₂CO₃ which could have been formed through the exposure of the TiO₂ to the electrolyte LiOH and atmospheric CO₂, the following experiment was carried out. The material after electroreduction was washed thoroughly with acetone several times till no further LiOH or Li₂CO₃ were detected as indicated by the color of the washings in the presence of phenolphthalein indicator. The resultant powder was dried and pressed back into a pellet and its XPS spectra recorded. As can be seen from fig. 5.9 b, the washing did reduce the intensity of the Li (1s) peak because of the removal of free LiOH and Li₂CO₃. However, shoulder of peak was still present suggesting that the material indeed was
Li_xTiO_2. Chauvat et al [18] have reported similar XPS data for the formation of Li_xTiO_2 in molten Li_2CO_3-Na_2CO_3 fuel cells.

![Graph](image)

**Fig. 5.9** The XPS spectra of Li (1s) of titanium dioxide (TiO_2) electroreduced at -496 mV: (a) before washing; (b) after washing with acetone.

### 5.3.2.3 Infra-red spectral studies

The infra-red spectra of TiO_2 material in the region 500 to 1000 cm\(^{-1}\) are shown in fig. 5.10. The broad peak at around 700 cm\(^{-1}\) for the material before the electroreduction, fig. 5.10 a, corresponds to a TiO_2 lattice vibration similar to that reported by Lee et al [19]. The spectra for the same material after electroreduction have a new peak at 600 cm\(^{-1}\) (fig. 5.10 b). Similar spectra were observed for LiTi_2O_4 by Picquart et al [20].
Fig. 5.10 FTIR spectra of titanium dioxide ($\text{TiO}_2$) cathode: (a) before; (b) after electroreduction at $-496$ mV.
5. 4 Conclusions

TiO\textsubscript{2} (anatase) undergoes electroreduction/oxidation in aqueous LiOH primarily by a Li\textsuperscript{+} intercalation mechanism. Some Ti\textsubscript{2}O\textsubscript{3} is also formed during electroreduction and thus the reduction/oxidation is not reversible. The discharge voltage of this material in a Zn/TiO\textsubscript{2}-aqueous LiOH battery is not suitable for TiO\textsubscript{2} being used as a cathode in aqueous battery systems.

5. 5 References


11. JCPDS cards: 16-223 and 10-63.


Chapter 6

Electrochemical behavior of LiFePO₄ in aqueous lithium hydroxide electrolyte

6.1 Introduction

As described in Chapter 2, LiFePO₄ has been developed as a cathode material for use in lithium batteries which use non-aqueous electrolytes [1-5]. Its electrochemical behavior corresponding to non-aqueous lithium batteries is widely reported in the literature [6-13]. For these batteries the electrochemical reaction of LiFePO₄ is generally represented as

\[
\text{charge} \quad \text{discharge} \\
\text{LiFePO}_4 \rightleftharpoons \text{FePO}_4 + \text{Li}^+ + \text{e}^- \\
\text{Eq. [6.1]}
\]

Reversible Li⁺ ion extraction/insertion (intercalation) occurs on charge/discharge of a LiFePO₄ cathode.

Since a major objective of this project is to establish whether such materials could also be used to develop other battery systems which might use aqueous lithium hydroxide electrolyte, the electrochemical behavior of LiFePO₄ has been investigated in aqueous LiOH. The focus of this work is on establishing the mechanism through which electrooxidation/reduction of this material occurs in aqueous LiOH electrolyte and how it compares with that known for the same in non-aqueous electrolytes. No report on investigation of LiFePO₄ in aqueous systems was found in the literature. The following sections describe the results of this work.
6.2 Experimental

The material LiFePO$_4$ (which contained 5 wt. % carbon to make it electrically conductive (Ch.2)) and FePO$_4$ (amorphous) were obtained from the University of Wollongong and Kyushu University, respectively. BDH analytical grade Zn foil (99.9%), Ajax chemicals reagent grade ZnSO$_4$.$7$H$_2$O and Sigma Chemicals reagent grade LiOH.$H_2$O were used as received. As described in Chapter 2, it is a common practice to add carbon at the beginning of the synthesis in order to provide sufficient conductivity.

The experimental procedures for the cyclic voltammetric studies were similar to those reported in Section 3.2. The potentials were measured against a standard calomel reference electrode and potentials reported as such. The electrolyte was a saturated aqueous solution of lithium hydroxide. The working electrode (LiFePO$_4$) was cycled between $-0.65$ V and $0.1$ V, each time starting at $-0.65$ V, going initially in the anodic direction.

An EG & G PAR Potentiostat/Galvanostat model 273A, operated by model 270 software (EG&G) was used to scan the potential at 25 $\mu$V/s in all experiments [14]. All electrochemical measurements were carried out at room temperature ($25 \pm 1^\circ$ C). The products formed during oxidation/reduction were characterized by a Siemens X-ray diffractometer using Philips Co K$_\alpha$ radiation. The SEM was performed on a scanning electron microscope (Philips Analytical XL series 20). X-ray photoelectron spectroscopy (Kratos Ultra Axis Spectrometer) using monochromatic Al K$_\alpha$ (1486.6 eV) radiation was carried out to analyze the chemical binding energy of the samples. The XPS analysis was started when the pressure in the analysis chamber fell below $1 \times 10^{-9}$ hPa. Carbon, C (1s), was used as a reference for all the samples. Secondary ion mass spectrometry (SIMS)
spectra were collected on a Cameca ims 5f instrument at the Australian Nuclear Science and Technology Organization (ANSTO), Lucas Heights, Sydney. An O$_2^+$ primary ion source (12.5 kV) was used to generate secondary ions. A primary beam of 50 nA was rastered over an area of 250 x 250 µm in all experiments. The SIMS negative ion signals corresponding to $^7$Li and $^{56}$Fe were recorded. An energy offset of -350 V was used to suppress molecular interferences on the peaks of interest.

6.3. Results and Discussion

6.3.1 Electrochemical behavior of LiFePO$_4$ in Zn/LiFePO$_4$-aqueous lithium hydroxide cell

The cell characteristics of Zn/LiFePO$_4$ using saturated LiOH containing 1 mol L$^{-1}$ ZnSO$_4$ as the electrolyte were investigated. The cell was galvanostatically charged first and then galvanostatically discharged at the same current density. The results are shown in fig 6.1. During the charge process there was a gradual increase in potential to the charge cutoff voltage of 1.8 V. During discharge, initially the voltage dropped approximately to 1.0 V and then gradually decreased to 0.7 V after which it dropped rapidly to the cutoff voltage of 0.4 V. The coulombic efficiency of the first cycle was calculated to be approximately 50 %.
Fig. 6.1 The first charge-discharge profile of Zn/LiFePO₄ cells using saturated aqueous LiOH containing 1 mol L⁻¹ of ZnSO₄ as the electrolyte at 0.25 mA/cm².

6.3.2 Cyclic voltammetric characteristics of LiFePO₄

Figure 6.2 shows a typical cyclic voltammogram of LiFePO₄. The scan was initiated at -630 mV going in the anodic direction to +100 mV and then reversing it to the starting potential. While only one oxidation peak A₁ (at -42 mV) occurs during the anodic going portion of the CV, two cathodic peaks C₁ (-490 mV) and C₂ (-370 mV) are observed during the reverse scan. These results suggests that

(a) The material undergoes only one oxidation process at -42 mV.

(b) The product formed during the oxidation process undergoes two separate reduction processes during the reverse cathodic scan.

In another experiment (fig. 6.3) the scan was initiated in the same way as before but the voltage was held constant for 30 and 60 minutes at the anodic limit (-42 mV) before reversing the scan. It was found that the peak heights of both C₁ and C₂ increased
Fig. 6.2 Cyclic voltammogram of LiFePO$_4$ in lithium hydroxide aqueous solution

Fig. 6.3 Effect of holding potential at $-42$ mV for various intervals time on the current-voltage profile of LiFePO$_4$ in aqueous LiOH (scan rate: $25 \mu$V.s$^{-1}$; potential limit: $-0.6$ to $0.1$ V and back).
with the length of time for which the electrode was held at $-42 \text{ mV}$. This confirms that the cathodic peaks ($C_1$ and $C_2$) corresponded to the reduction of the material formed during oxidation of LiFePO$_4$ at $-42 \text{ mV}$. The characterization of the products formed during oxidation/reduction is described in section 6.3.3.

### 6.3.3 Physical characterization of LiFePO$_4$ and the products formed during cell charge/discharge and cyclic voltammetric investigations

Figure 6.4 shows the SEM photographs of the as-received LiFePO$_4$ powder in different magnifications indicating that the particles had an average size of 1-2 $\mu\text{m}$.

Fig. 6.4 SEM micrograph of LiFePO$_4$ powders
The X-ray diffraction spectrum of the LiFePO₄ material is shown in fig. 6.5. The spectrum is similar to that reported by Bewlay et al [5]. It consists of peaks at \( \theta = 19.35^\circ, 23.9^\circ, 26.1^\circ, 29.5^\circ, 34.4^\circ, 35.3^\circ, 38.19^\circ, 42.16^\circ, 43.25^\circ, 44.87^\circ \) and \( 47.05^\circ \). These data match those reported in the literature for LiFePO₄ [1, 5] indicating that the material was crystalline of orthorhombic structure.

![X-ray diffraction pattern](image)

**Fig. 6.5** X-ray diffraction pattern of the lithium iron phosphate (5 wt% carbon included) as received from University of Wollongong.

The X-ray diffraction spectra of the starting material LiFePO₄ and those of the products formed on its electrooxidation together with that of the materials formed on subsequent electroreduction are shown in fig. 6.6.

The spectrum of the material formed on electrooxidation of LiFePO₄ (fig. 6.6 b) consists of peaks at \( \theta = 35.52^\circ, 38.47^\circ, 42.45^\circ, 43.57^\circ, 45.16^\circ \) and \( 47.41^\circ \). These data
match those for FePO₄ reported in the literature [1] which indicates that FePO₄ is formed on oxidation of LiFePO₄. Thus the oxidation of LiFePO₄ in aqueous LiOH involves de-intercalation of Li⁺ and hence the mechanism resembles that in non-aqueous solvents reported by Padhi et al [1].

![XRD patterns](image)

**Fig. 6.6** XRD patterns showing the changes occurring during the redox process in aqueous solutions (a) before electrochemical treatment, (b) after oxidation and (c) after reduction.

The spectra of the material formed on subsequent reduction of the product formed on oxidation of LiFePO₄ (fig. 6.6 c) consists of peaks at 2θ = 35.02, 37.95, 41.93, 43.10, 44.65 and 46.95 which indicates that LiFePO₄ is reproduced. This result is similar to that
reported by Padhi et al [1] for non-aqueous media. A careful examination of fig. 6.6 c indicates that there is evidence of the presence of a peak at $2\theta = 35.02^\circ$, which could be assigned to $\text{Fe}_2\text{O}_3$. Thus, the oxidation of $\text{LiFePO}_4$ yields $\text{FePO}_4$. Subsequent reduction of $\text{FePO}_4$ produces a mixture of $\text{LiFePO}_4$ and $\text{Fe}_2\text{O}_3$. The oxidation of $\text{LiFePO}_4$ in aqueous $\text{LiOH}$ is therefore not fully reversible as is the case in non-aqueous media.

Figure 6.7 shows the X-ray photoelectron spectra of the Li (1s) region of $\text{LiFePO}_4$ before and after oxidation and subsequent removal of free $\text{LiOH}$ and $\text{Li}_2\text{CO}_3$ by washing as described above. The sample before oxidation (fig. 6.7 a) is characterized by a peak with a high intensity at 55.3 eV for the oxidized sample (fig. 6.7 b) appears as a shoulder with much reduced intensity. This indicates that $\text{Li}^{+}$ is extracted from $\text{LiFePO}_4$.

**Fig. 6.7** XPS spectra of Li (1s) of $\text{LiFePO}_4$: (a) before and (b) after oxidation.
during oxidation. Figure 6.8 shows the XPS spectra of the Fe (2p) region of LiFePO$_4$ before and after oxidation. The Fe (2p) with spin-orbit splitting components of 2p$_{1/2}$ at 710.6 and 2p$_{3/2}$ at 724 eV can be seen in the figure. After oxidation there is a clear change in the Fe line shape. The chemical shift towards higher binding energy can be attributed to the oxidation of Fe(II) to Fe(III) [16].

![Fig. 6.8 XPS spectra of Fe (2p) of LiFePO$_4$: (a) before and (b) after oxidation](image)

For further confirmation of extraction/insertion processes of Li$^+$ in the host structure of LiFePO$_4$, secondary ion mass spectrometry (SIMS) could not be carried out by dynamic SIMS because the discharged cathode was found to be covered with a thick layer of Li$_2$CO$_3$ which as noted earlier in the thesis would have been formed through the
reaction of LiOH by the atmospheric CO₂. The presence of Li₂CO₃ on the cathode surface was confirmed from the following SEM, XPS and IR results (figs. 6.9-6.11). The change in morphology of the material on discharge of LiFePO₄ could be seen from fig. 6.9.

Fig. 6.9 Scanning electron micrographs of the LiFePO₄ (a) before any electrochemical treatment (b) after discharge (c) discharged sample washed thoroughly in acetone and then with water.
The material after discharge was washed thoroughly as described earlier with acetone several times until no further Li\(^+\) ions were detected in the washing liquid and the SEM of the sample was recorded. The SEM of this material is also shown in fig. 6.9 c. The image of the washed sample had morphology very different from that of the material before washing. The presence of lithium carbonate on the discharged cathode surface is further confirmed via XPS and FTIR results shown in figs. 6.10 and 6.11 respectively.

![Graph showing XPS spectra of C 1s for cathode LiFePO\(_4\) after discharge](image)

Fig. 6.10 XPS spectra of C 1s for the cathode LiFePO\(_4\) after discharge

The important feature to notice in XPS spectra (fig. 6.10) is the presence of a highly dominant carbonate peak in the C (1s) region and lithium which is attributed to Li\(_2\)CO\(_3\) for the sample before washing. Consideration of the binding energies [16] and relative concentrations suggests that the electrode material before washing was covered
extensively with a mixture of LiOH and Li$_2$CO$_3$ (as evidenced by the SEM fig. 6.9 b). These results are further confirmed by FTIR spectra (fig 6.11). As shown in fig. 6.11, before washing the IR band at 1450–1500 cm$^{-1}$ indicates the presence of Li$_2$CO$_3$. After washing, the absence of a peak in this region indicates the absence of carbonate.

![FTIR Spectra](image)

**Fig. 6.11** FTIR Spectra of the discharged LiFePO$_4$ material before and after washing. The material before washing clearly indicates the presence of the IR band at 1450-1500 cm$^{-1}$ which is the characteristic of Li$_2$CO$_3$.

The washed pellet was mounted in the SIMS apparatus and analysis undertaken. The SIMS signal was used to determine the percentage of lithium present before and after electrochemical treatment rather than traditional depth profiling.

One such set of SIMS data is shown in fig. 6.12. This figure shows changes in the Li/Fe ratio as obtained by secondary ion mass spectroscopic analysis of the products formed on oxidation/reduction of LiFePO$_4$. As can be seen from this data the Li/Fe ratio
decreased during oxidation and then increased during the reverse electroreduction process. All the above studies indicate that lithium ion deintercalation/intercalation occurred when LiFePO$_4$ was subjected to electrooxidation/reduction.

![Graph showing Li/Fe ratio before and after electrochemical treatment.](image)

**Fig. 6.12** SIMS isotopic mass ratio of LiFePO$_4$

6.4 Conclusions

The electrochemical oxidation of LiFePO$_4$ in saturated aqueous lithium hydroxide (LiOH) electrolyte results in the formation of delithiated product FePO$_4$ similar to that for non-aqueous media. The reverse reduction of FePO$_4$ however is not fully reversible as it
forms a mixture of LiFePO$_4$ and there is an indication of Fe$_2$O$_4$ formation also. In this regard LiFePO$_4$ behaves quite differently from that in non-aqueous electrolytes. Thus this material is not suitable for use as a cathode in aqueous battery systems.

6.5 References


Chapter 7
Electrochemical behavior of LiMnPO₄ in aqueous lithium hydroxide electrolyte

7.1 Introduction

In Chapter 6, the electrochemistry of LiFePO₄ as a battery cathode material in aqueous lithium hydroxide electrolyte was discussed. This motivated a search for other transition metal olivine compounds like LiMnPO₄ which might be suitable for use as battery cathodes in aqueous LiOH electrolyte. The use of LiMnPO₄ as a lithium battery cathode material in non-aqueous lithium solutions has been investigated by Padhi et al [1]. His work suggested that lithium insertion/extraction into the host structure of this olivine-type compound occurred during discharge/charge cycles of the battery. This chapter describes an investigation of the electrochemical behavior of LiMnPO₄ in aqueous lithium hydroxide electrolyte. The focus of this work is to determine the mechanism through which LiMnPO₄ undergoes electron transfer reactions in aqueous LiOH and how does it compare with that in non-aqueous lithium ion electrolytes.

7.2 Experimental

The LiMnPO₄ (10 wt% carbon included) was received from Tokyo Institute of Technology. Analytical grade Zn foil (99.9%) from BDH chemicals and reagent grade LiOH.H₂O from Sigma Chemicals Company were used as received.

The procedures and equipment used for investigation of the electrochemistry of LiMnPO₄ and material characterizations were the same except for the current density as those noted in Chapter 6 for LiFePO₄.
7.3 Results and Discussion

7.3.1 Electrochemical behavior of LiMnPO$_4$ in Zn/LiMnPO$_4$–aqueous lithium hydroxide cell

The characteristics of the Zn|LiOH, ZnSO$_4$|LiMnPO$_4$ cell were investigated by first charging followed by discharging galvanostatically at 0.5 mA/cm$^2$. During the charge process there was a gradual increase in potential to the charge cutoff voltage of 1.9 V (fig. 7.1). During the discharge process, there was an initial sharp drop in voltage from 1.5 to 1.2 followed by a steady decrease in potential. The coulombic efficiency of the first cycle was 80 %. The voltaic efficiency of the first cycle was 65 %.

![Graph showing charge and discharge](image)

**Fig. 7.1** Charge / discharge profile of Zn/LiMnPO$_4$ cells using saturated aqueous LiOH containing 1mol L$^{-1}$ of ZnSO$_4$ electrolyte at 0.5 mA/cm$^2$ (first cycle).
The coulombic efficiency as a function of cycle number is shown in Fig. 7.2. It dropped rapidly during the first few cycles after which the decrease was gradual.

![Graph showing coulombic efficiency vs. cycle number.](image)

**Fig.7.2** Coulombic efficiency vs. cycle number of Zn/LiMnPO$_4$ cells using saturated aqueous LiOH containing 1 mol L$^{-1}$ of ZnSO$_4$ electrolyte at 0.5 mA/cm$^2$ current density.

7.3.2 Voltammetric behavior of LiMnPO$_4$

The redox behavior of LiMnPO$_4$ can be seen from the cyclic voltammogram in the potential region $-0.65$ to $0.1$ V in Fig. 7.3. The scan was initiated at $-630$ mV going first in the anodic direction to $+100$ mV and then reversing it to the starting potential at a scan rate $25\mu$V/s. An oxidation peak $A_1$ is seen at $65$ mV in the anodic portion of the CV.
Fig. 7.3 A typical cyclic voltammogram of LiMnPO₄ in saturated aqueous lithium hydroxide solution.

A cathodic peak C₁ is observed at –480 mV during the reverse scan. Thus the material undergoes electrooxidation/reduction corresponding to change of the oxidation state of the Mn atom in LiMnPO₄. The large gap between the oxidation and reduction potentials is because of the high overpotential of the oxidation/reduction reactions. This is hardly surprising given the huge changes in crystal morphology as seen in Fig. 7.7.
7.3.3 Physical characterization of LiMnPO$_4$ and the products formed during cell charge/discharge and cyclic voltammetric investigation

With the objective of identifying the products formed on electrooxidation and reverse reduction, the following experiment was performed. The material was subjected to electrooxidation in a three cell configuration under galvanostatic conditions (0.5 mA/cm$^2$). The products formed were examined by XRD, SEM, XPS and SIMS. The electrooxidized material was then subjected to reverse reduction galvanostatically at the same current density. The resulting material was also analyzed by using the same techniques as noted above.

The X-ray diffraction spectrum of the material (LiMnPO$_4$) before any electrochemical treatment is shown in fig.7.4.

![X-ray diffraction spectrum](image)

**Fig. 7.4 X-ray diffraction spectrum of the LiMnPO$_4$ powder**
The data matched the single-phase orthorhombic (olivine) structure as reported in the literature [1-3]. The SEM photograph of the as-received LiMnPO₄ powder indicates that the particle size was 2-5 µm as seen from fig. 7.5.

![SEM micrograph of the starting material LiMnPO₄ powder](image)

**Fig. 7.5** SEM micrograph of the starting material LiMnPO₄ powder

A comparison of the X-ray diffraction spectra of the starting material LiMnPO₄ before oxidation and that of the product formed on its electrooxidation is shown in fig. 7.6. The XRD spectrum of the oxidized material differs significantly from that of the starting material. New reflections at 2θ = 22.5°, 35.0° and 42.0° are seen. These peaks are assigned to MnPO₄ in accordance with the values quoted in the ICDD card No: 70-0180.
Fig. 7.6 X-ray diffraction spectra of LiMnPO₄ (a) before and (b) after electrooxidation

The XRD pattern of the electrooxidized material is indicative of low crystallinity of the product which in this case is delithiated MnPO₄. This is also reflected in the scanning electron micrograph (SEM) of this material as shown in fig. 7.7. The product has a very different morphology compared to the material before the oxidation (fig. 7.7).
Fig. 7.7 SEM images of LiMnPO$_4$ before and after electrooxidation/reduction
Fig. 7.8 X-ray diffraction spectra of LiMnPO$_4$ (a) before electrooxidation (b) after electrooxidation and (c) after reverse electroreduction.

Figure 7.8 shows variation of the XRD pattern of the materials (a) before electrooxidation (b) after electrooxidation and (c) after reverse electrooxidation of LiMnPO$_4$. The XRD pattern (fig. 7.7 c) now matches that of the original raw material which had not been subjected to any electrochemical treatment (fig. 7.8 a). This is also reflected in the morphology of the SEM micrograph (after reduction) in fig. 7.7. This suggests that the electrooxidation of LiMnPO$_4$ is reversible and that oxidation of LiMnPO$_4$ forms MnPO$_4$ which on subsequent reduction reverts back to LiMnPO$_4$. 

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Thus the oxidation/reduction of LiMnPO$_4$ in aqueous LiOH involves delithiation/lithiation mechanism which is similar to that in non-aqueous solvents reported by Delacourt et al [4] and Li et al [5].

The IR spectra of LiMnPO$_4$ before and after oxidation are shown in Fig. 7.9. The LiMnPO$_4$ material before oxidation showed absorption peaks around 600 cm$^{-1}$ and 1100 cm$^{-1}$ corresponding to M-O stretching and P-O stretching respectively. An IR absorption peak around 1600 cm$^{-1}$, attributed to H-O-H bending mode of crystal water, was detected in LiMnPO$_4$ sample alone. The spectrum of the electrooxidized material was almost identical indicating that Li$^+$ intercalation does not change the host lattice.

![FTIR spectra of LiMnPO$_4$](image)

**Fig. 7.9** FTIR spectra of the LiMnPO$_4$ electrode before and after oxidation. Peak regions A: M-O stretching; B: P-O stretching; and C: H-O-H Bending

Figure 7.10 shows the XPS spectra of the Li (1s) and Mn (3s) region for the LiMnPO$_4$ material (a) before electrochemical treatment, (b) after electrooxidation and (c)
Fig. 7.10 XPS spectra of Mn 3s and Li 1s of LiMnPO₄ (a) before electro-oxidation (b) after electrooxidation and (c) after reverse electroreduction.

after electrochemical reduction of the material following to the electrooxidation. The peaks at 48.7 eV and 56.4 eV correspond to Mn (3s) and Li (1s) respectively [6]. The peak at 48.7 eV corresponding to Mn (3s) is present in all the three samples (fig 7.10), whereas the peak at 56.4 eV corresponding to Li (1s) is high in sample (a) and (c) but very low for sample (b). This confirms that on electrooxidation, Li⁺ is removed from LiMnPO₄ and is re-inserted into MnPO₄ after the material has been reduced back. This result provides further evidence of reversible delithiation of LiMnPO₄ on oxidation.

Further confirmation of delithiation/lithiation of Li⁺ during oxidation/reduction of LiMnPO₄ is obtained from secondary ion mass spectrometry (SIMS) analysis. The figure
Fig. 7.11 SIMS Li ion count of LiMnPO₄.

7.11 shows changes in the Li⁺ ion count within ± 2 as obtained by SIMS analysis of the products formed on oxidation of LiMnPO₄ and its reverse reduction. The data show that the Li⁺ count in the material formed on oxidation is lower than that before oxidation. The count increases when this material is reduced back to its original form. This supports the delithiation mechanism for oxidation/reduction of LiMnPO₄.

Based upon the results discussed above, it can be concluded that the electrochemical oxidation/reduction of LiMnPO₄ is reversible.
7.4 Conclusions

The electrochemical investigation of LiMnPO₄ as a cathode material in aqueous LiOH shows that MnPO₄ is formed when LiMnPO₄ is electrooxidized and the process is reversible. The voltaic efficiency and coulombic efficiency of LiMnPO₄ in Zn/LiMnPO₄-aqueous LiOH battery are only slightly lower than that of EMD noted in Chapter 3. Thus this material has potential for being used as a cathode material in aqueous battery systems containing LiOH electrolyte.

7.5 References


Chapter 8

Conclusions and Recommendations for Future Work

This thesis describes the results of an investigation of the electrochemical behavior of MnO₂, TiO₂, LiFePO₄ and LiMnPO₄ in aqueous LiOH electrolyte. The emphasis of the work has been to identify the mechanism through which electron transfer reactions occur in the presence of aqueous electrolyte as compared to the known behavior of these materials in non-aqueous electrolytes in relation to their use in lithium batteries. One of the objectives has been to determine whether any of these materials could be used as a cathode material in aqueous battery systems. The main conclusions of this study and recommendations for future work are outlined in this chapter.

Conclusions

Electrolytic manganese dioxide (EMD) and the chemically prepared battery grade variety (BGM) of the same material both undergo oxidation/reduction in aqueous LiOH electrolyte through a Li⁺ intercalation mechanism. This is similar to that known for their behavior in non-aqueous electrolyte as is usually used in lithium batteries. The mechanism of electroreduction/oxidation of MnO₂ in aqueous LiOH is very different from its known mechanism involving H⁺ ions in aqueous KOH electrolyte. The electrode potential of the MnO₂/LiMnO₂ couple battery is 3 V, when used as a cathode material in Zn/MnO₂- aqueous LiOH is 1.1 V vs. SCE. The BGM-based battery discharges at a voltage higher than that which uses EMD. For the first cycle the voltaic efficiency for the battery with BGM was 86% as compared to 83% for EMD at 0.5 mA/cm². However, the
rechargeability of the EMD battery is superior to that of the BGM battery. Only EMD material has the potential for developing rechargeable aqueous Li⁺ electrolyte battery systems.

$\text{TiO}_2$ (anatase) undergoes electroreduction and oxidation in aqueous LiOH primarily by Li⁺ intercalation mechanism. Some $\text{Ti}_2\text{O}_3$ is also formed during electroreduction and thus the reduction/oxidation is not reversible. However, the discharge voltage of Zn/TiO₂-aqueous LiOH battery is very low. Thus TiO₂ is not suitable for use in this aqueous battery system.

LiFePO₄ (olivine-type structure) undergoes electrooxidation in aqueous LiOH forming FePO₄. However the subsequent reduction forms not only the original LiFePO₄ but also Fe₃O₄. Thus electrooxidation/reduction is not completely reversible. In this regard, LiFePO₄ behaves quite differently from that in non-aqueous media and is not a suitable material for use as a cathode in aqueous battery systems.

LiMnPO₄ (olivine-type structure) undergoes electrooxidation in aqueous LiOH forming MnPO₄ which is reversible. After the charge cycle, the subsequent discharge at 0.5 mA/cm², the voltage of the Zn/MnPO₄ - aqueous LiOH battery decreases rapidly from 1.5 to 1.2 V and then decreases gradually. The decrease in voltage is lower than that for the various MnO₂ materials investigated in this thesis.
Recommendations for future research

The work described in this thesis suggests that electrolytic manganese dioxide (EMD) and LiMnPO$_4$ should be suitable candidates for use in rechargeable batteries which use aqueous lithium hydroxide as electrolyte. It is, however, important to note that only laboratory scale batteries were investigated in this work. Before commercial applications can be considered, further work is needed to improve the coulombic and voltaic efficiencies together with the cycle life of the materials. Some recommendations for further work, not in any particular order, are listed below:

1. Carry out further research on the influence of various additives into MnO$_2$ cathode material to improve the cell performance. Some doping materials such as TiS$_2$, TiB$_2$, TiO$_2$ and Bi$_2$O$_3$ are known to stabilize the MnO$_2$ lattice towards dimensional changes that occur during the discharge process [1-2].

2. Examine the effect of heating on structural modification of γ-MnO$_2$ and its consequent effect on the electrochemical behavior of γ-MnO$_2$ as a cathode material.

3. Examine the use of lithium chloride as an alternative to lithium hydroxide electrolyte. LiCl is stable to air and is much less corrosive than LiOH.

4. Investigate the effect of adding carbon black in various proportions to the cathode material during electrode preparation.

5. Examine other MnO$_2$ materials (international common samples) for suitability in rechargeable aqueous battery systems.
6. Examine the influence of dopant ions (e.g. cobalt) substitution in various proportions in LiMnPO₄ and MnO₂ cathode materials to improve cell performance [3-5].

References

Appendix

Pages on the papers published based on the results of this thesis

(A) Journal Publications
Lithium insertion into manganese dioxide electrode in $\text{MnO}_2/\text{Zn}$ aqueous battery 
Part I. A preliminary study

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Received 12 November 2003; accepted 10 December 2003

Abstract

The discharge characteristics of manganese dioxide ($\gamma$-$\text{MnO}_2$ of electrolytic manganese dioxide (EMD type)) as a cathode material in a Zn–$\text{MnO}_2$ battery containing saturated aqueous LiOH electrolyte have been investigated. The X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) data on the discharged material indicate that lithium is intercalated into the host structure of $\text{EMD}$ without the destruction of its core material. The XPS data show that a layer of insoluble material, possibly Li$_2$CO$_3$, is deposited on the cathode, creating a barrier to $\text{H}_2\text{O}$, thus preventing the formation of Mn hydroxides, but allowing the migration of Li ions into the $\text{MnO}_2$ structure. The cell could be reversibly charged with 83% of voltaic efficiency at 0.5 mA/cm$^2$ current density to a 1.9 V cutoff voltage. The percentage utilization of the cathode material during discharge was 56%.

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Keywords: Aqueous battery; Lithium insertion; $\text{MnO}_2$; Electrolyte; XRD; XPS

I. Introduction

Materials with the general formula $\text{LiMO}_2$ ($\text{M} = \text{Mn, Fe, Ni, Co}$) [1–4] have received a great deal of attention recently as prospective cathode materials for use in a non-aqueous cell. Of the four transition metals above, Mn and Fe are by far the most attractive with regard to toxicity concerns and from an economic point of view. Manganese has an added advantage in that it can support higher oxidation states, which makes it suitable as a cathode material. Manganese dioxide is also used as the positive active (cathode) material in Leclanche and alkaline manganese batteries [5], which together dominate the primary battery market. Electrolytic manganese dioxide (EMD) is one of the most important materials for both aqueous and non-aqueous cells. Extensive research [6] has been done on lithium insertion into $\gamma$-$\text{MnO}_2$ of EMD type in non-aqueous cells. Intercalation of Li$^+$ ions into host $\gamma$-$\text{MnO}_2$ structures is widely reported [6,7] in non-aqueous batteries. There is very limited information on intercalation occurring in aqueous media [8]. If this mechanism is possible in aqueous media the $\text{MnO}_2$ cathode could become rechargeable similar to non-aqueous Li–$\text{MnO}_2$ batteries. Hence, it could open up a new field of rechargeable alkaline batteries that utilize $\text{MnO}_2$ as the cathode active material. With this in mind, we have investigated the use of lithium hydroxide (LiOH) in place of traditional potassium hydroxide as the battery electrolyte in alkaline Zn–$\text{MnO}_2$ batteries. The main objective of this work is to investigate whether intercalation of Li$^+$ into the host structure of $\text{MnO}_2$ does occur. Other objectives of this work are:

- the effect of LiOH on $\text{MnO}_2$ utilization and voltaic efficiency;
- the electrochemical characteristics and the discharge mechanism of $\text{MnO}_2$ as a cathode material.

2. Short review of $\gamma$-$\text{MnO}_2$ as a cathode material

Synthetic manganese dioxides and particularly those made by electrodeposition (EMD) are used in high performance batteries. EMD is a member of the imperfectly crystalline $\gamma$-manganese dioxides [9], which are related to ramsdellite and pyrolusite by various proportions of the
types of random structural disorder [10], de Wolff disorder and microtwinning, γ-MnO₂ shows a high complexity in its chemical composition as well as in its crystallographic structure. Among the different models proposed to account for the γ-MnO₂ for a practical battery system [11], Ruetschi’s model [12] presents a quantitative report in the cation vacancy in MnO₂. In the Ruetschi’s lattice-vacancy model of γ-MnO₂, it is considered that

1. Each manganese ion in the MnO₂ structure is octahedrally co-ordinated to six nearest oxygen ions, and each oxygen ion is co-ordinated to three nearest manganese ions. The MnO₆ octahedral are arranged in the crystal as to share edges and corners. Since the ionic radii of O²⁻ ions (1.40 Å) are much larger than Mn⁴⁺ ions (0.53 Å) the lattice resembles a dense packing of O²⁻ ions, with the small Mn⁴⁺ ions orderly arranged in the edge shared MnO₆ octahedral chains between O²⁻ layers [13]. This is the usual crystallographic description.

2. In this structure, a fraction of Mn⁴⁺ ions are missing in the Mn⁴⁺ sub-lattice. Each empty Mn⁴⁺ site is, for charge compensation, coordinated to four protons, the latter being present in the form of OH⁻ ions. The OH⁻ ions replace O²⁻ in the lattice without significant volume change of the unit cell, the ionic radii of O²⁻ and OH⁻ being very similar [14]. Normal unit cell parameters are thus maintained.

3. A fraction of the Mn⁴⁺ ions are replaced by Mn³⁺. For each Mn³⁺ present, one proton is introduced for charge compensation. These protons for further OH⁻ ions, replacing O²⁻ in the lattice.

4. Thus the lattice is composed of O²⁻, OH⁻, Mn⁴⁺ and Mn³⁺ ions and Mn vacancies. All the structural water is present in the form of OH⁻ ions, associated with either Mn vacancies, or Mn³⁺ ions.

The γ-MnO₂ can be described by the chemical formula Mn^{(1−x−y−z)}O^{(x+y+z)}OH^{−y}O^{2−}OH^{−x} where y is the cation vacancy fraction and Z the fraction of Mn⁴⁺ ions replacing Mn⁴⁺ in the manganese sub-lattice. The electrochemical reactions that take place at the manganese dioxide electrode in aqueous cell [15] during the discharge process of a battery corresponding to the insertion of X can then be described by the following equations:

For \( x > 1 − Y − Z \)

\[
\text{Mn}_{(1−Y−Z)}(\text{OH})_{(4Y+Z)} + X \text{H}^{+} + X \text{e}^{−} \rightarrow \text{MnO}_{2−x}(\text{OH})_{x}
\]

(2)

For \( x > 1 − Y − Z \)

\[
\text{Mn}_{(1−Y−Z)}(\text{OH})_{(4Y+Z)} + X \text{H}^{+} + X \text{e}^{−} \rightarrow \text{MnO}_{2−x}(\text{OH})_{x}
\]

(3)

The products of the materials produced after discharge in Eq. (3) is known to be electrochemically inactive, so this held as primary aqueous batteries.

In the non-aqueous lithium cells during discharge, lithium ions are inserted into the vacant sites while the Mn⁴⁺ ions are replaced by Mn³⁺ ions, which explains the electrochemical behavior of γ-MnO₂ associated with the discharge of Li-MnO₂ batteries [7]. The electrochemical reactions for non-aqueous lithium cells have been generally written as

\[
\text{MnO}_2 + \text{Li}^+ + \text{e}^{−} \rightarrow \text{LiMnO}_2
\]

(4)

3. Experimental

The γ-MnO₂ of EMD type used in this work was purchased from the Foote mineral company. The X-ray diffraction pattern of the raw material indicated that it consisted of poorly crystallized γ-MnO₂. The theoretical maximum electrochemical capacity deliverable per unit weight for a one-electron process is 289 mAh/g.

The materials employed during electrode preparation were Zn metal for the anode and γ-MnO₂ for the cathode. The MnO₂ active material was first mixed with 20 wt.% of carbon black and with 10 wt.% of PVDF as a binder and then pressed into a disk shape with a diameter of 12 mm. Each disk was 0.5 mm thick and weighed approximately 35 mg. An electrochemical test cell was constructed with the disk as the cathode, Zn metal as the anode and filter paper as the separator. The mass of zinc was at least 10-fold in excess of that required for the stoichiometric reaction between Zn and MnO₂. The electrolyte was a saturated solution of lithium hydroxide (LiOH) containing 1 mol/l−1 zinc sulfate (ZnSO₄). Analytical reagent grade of zinc sulfate heptahydrate (ZnSO₄·7H₂O; Ajax Chemicals), lithium hydroxide monohydrate (LiOH·H₂O; Sigma Chemicals company) and potassium hydroxide (KOH; Ajax Chemicals) were dissolved in deionized water to prepare solutions of required concentrations.

The cells were charged/discharged galvanostatically at 0.5 mA/cm² by using an EG&G Princeton Applied Research Potentiostat/Galvanostat model 273A, operated by model 270 software (EG&G). The cutoff discharge and charge voltages were 1.0 and 1.9 V, respectively. All electrochemical measurements were carried out at ambient room atmosphere (25 ± 1°C).

The products formed during charge and discharge cycles were characterized by a Siemens X-ray diffractometer using Philips Co Ko radiation. X-ray photoelectron spectroscopy (Kratos Ultra Axis Spectrometer) using monochromatic Al Kα (1486.6 eV) radiation was used to analyze the chemical
binding energy of the samples. The XPS analysis was started when the pressure in the analysis chamber fell below $1 \times 10^{-9}$ hPa.

4. Results and discussion

4.1. Performance characteristics of Zn–MnO$_2$-aqueous LiOH cell

There is substantial literature on the performance characteristics of MnO$_2$ in alkaline aqueous Zn–MnO$_2$ cells using potassium hydroxide (KOH) as the electrolyte. The use of highly conductive potassium hydroxide as the electrolyte, results in a lower internal resistance [16]. However, the conductivity of the electrolyte is changed by the dissolution of Zn(OH)$_2$ from the anode during the discharge cycle. Kordestani et al. [17] has reported that the discharge behavior of the cathode material, MnO$_2$, in the alkaline KOH electrolyte occurs in an heterogeneous phase reaction, i.e. MnO$_2$ being converted to Mn$_2$O$_3$. Hence, the MnO$_2$ lattice expands and, at a certain point of discharge, the mechanism changes to an irreversible portion of the MnO$_2$ reduction process. To understand the effect of replacing KOH with LiOH in Zn–MnO$_2$ cell, we have carried out discharge cycles on two identical cells, both containing 1 M ZnSO$_4$, but one containing saturated KOH and the other LiOH aqueous solution. The results for the first discharge cycle for both the cells are shown in Fig. 1. It can be seen that the discharge curve for the cell with KOH is quite different from that of the LiOH cell (Fig. 1(a) and (b)). The cathode utilization for the KOH cell was 41% (120 mAh/g) as compared to 56% (162 mAh/g) for the LiOH cell using a 1 V cutoff for both cells. The discharge capacity for LiOH, Fig. 1(b), was higher and the decrease in cell potential was lower when LiOH was the electrolyte. For the KOH, the potential underwent a sharp fall at 1.0 V.

The reversibility of the cell Zn–MnO$_2$ using saturated aqueous LiOH containing 1 mol$^{-1}$ of ZnSO$_4$ as the electrolyte was investigated and the results are shown in Fig. 2. The cell could be reversibly discharged and charged. As can be seen in Fig. 2, the shape of the discharge curve is characterized by a sharp drop in voltage to 1.3 V, and a gradual downward-sloping potential profile until the 1 V cutoff voltage is reached. The cathode material utilization was calculated from the initial weight of the active MnO$_2$ in the cathode and the voltaic efficiency from the observed average charge/discharge voltages. The material utilization of 56% (162 mAh/g) and the voltaic efficiency of 83% were obtained. During the charge/discharge cycle, the cell potential changed continuously, indicating a homogenous phase reaction.

4.2. Characterization of the cathode material

In order to determine the mechanism by which the cathode material γ-MnO$_2$ discharges in Zn–MnO$_2$ cell in LiOH electrolyte, characterization of the discharged cathode material produced was investigated by XRD and XPS. Fig. 3(a) and (b) shows the X-ray diffraction patterns of the cathode material γ-MnO$_2$ before and after discharge. Due to the poor crystallinity of the cathode material, the X-ray diffraction pattern in Fig. 3(a) shows a few broad Bragg reflections. As can be seen in Fig. 3(b), an evolution of a new sharp peak at a d-spacing of 3.27 Å, and the corresponding shoulder at a d-spacing of 3.18 Å is observed in the discharged γ-MnO$_2$ material. Clearly, these peaks do not correspond to any of
the MnOOH structure, Mn$_2$O$_3$ or Mn$_3$O$_4$ which are reported to be formed when aqueous KOH based Zn/MnO$_2$ cells are discharged. This suggests that the discharge mechanism of this cathode material is not the same as that commonly reported for alkaline Zn–MnO$_2$ batteries. A close examination of our data suggests that the peaks correspond to those reported for non-aqueous lithium cells by Aurbach and coworkers [18]. The peaks corresponding to the d-spacing of 3.27 and 3.18 Å can be assigned to lithium intercalated γ-β-MnO$_2$ (a hexagonal close-packed arrangement of oxygen, in which Mn and Li ions are located at octahedral sites), and the co-existence of two phases. The MnO$_6$—octahedral structure includes tunnels (1 × 1) and (1 × 2) in which Li ions should intercalate/de-intercalate during discharge/charge process. Moreover, a comprehensive study of the intercalation mechanism by Ohzuku et al. [19] showed a similar diffraction peak at a d-spacing of 3.27 Å for their heat-treated γ-MnO$_2$ during the discharge in a non-aqueous lithium cell, and ascribed it to γ-β-MnO$_2$. Fig. 3(c) also shows the X-ray diffraction pattern of the cathode material after recharging the discharged battery. A decrease in the intensity of the peak corresponding to the γ-β-MnO$_2$ occurs. Hence, we can infer that the lithium intercalation is electrochemically reversible. However, it should be noted that the peak shifts to a lower angle. This is to be expected as the lithium ion is de-intercalated from the structure [20].

The cathode material formed during the discharge cycle was further characterized by X-ray photoelectron spectroscopy (XPS), a powerful tool for surface studies. A wide scan XPS spectrum of the surface (0–1400 eV) of this material is shown in Fig. 4. The important feature to notice in Fig. 4 is the highly dominant O 1s peak, while the signals of other elements of interest are quite weak. The surface of the cathode material was covered with a thick overlayer of material deposited during the discharge of the battery. This outer layer contained the elements C, O, and Li. H cannot be detected with XPS. Consideration of the binding energies and relative concentrations suggests that this overlayer was composed of a mixture of LiOH and Li$_2$CO$_3$. This outer layer required 5 h of ion bombardment (4.0 kV, 2 μA, 500 μA spot) to remove it and reveal the underlining material. We estimate the thickness of this material as 0.5 μm (assuming an etch rate of 1.7 nm/min). The XPS spectrum of the material after prolonged etching for 5 h (shown full scale, Fig. 5) reveals the presence of the underlying elements Zn, Mn, and Li, with a much reduced intensity of O 1s. It is interesting to note that Zn was not seen on the undisturbed outer surface, but is present in the active surface of the MnO$_2$ material. This is the clear evidence that the overlayer is porous with ions. These can travel through the overlayer to the active MnO$_2$ material underneath. Li$_2$CO$_3$ is insoluble. Fig. 6 shows the variation in concentration of the Li$_2$CO$_3$ and LiOH with depth. It is clear that the insoluble Li$_2$CO$_3$ forms a barrier to H$_2$O, but that the LiOH is able to move through the structure. The concentration of LiOH falls with depth into the solid in a profile that is not inconsistent with a diffusion driven process.

In order to view the spectra associated with each of the elements presented in Fig. 5, the XPS spectra over regions specific to elements of interest were recorded over five sweeps. Figs. 7–10 show the high resolution XPS spectra, as a function of argon ion etching of the material. It can be seen
Fig. 7. XPS spectra of O 1s for the cathode manganese dioxide (γ-MnO₂) after electrochemical lithium intercalation, time in figure indicates the etching duration.

Fig. 8. XPS spectra of C 1s for the cathode manganese dioxide (γ-MnO₂) after electrochemical lithium intercalation, time in figure indicates the etching duration.

Fig. 9. XPS spectra of Li 1s and Mn 3s for the cathode manganese dioxide (γ-MnO₂) after electrochemical lithium intercalation, time in figure indicates the etching duration.

Fig. 10. XPS spectra of Mn 2p for the cathode manganese dioxide (γ-MnO₂) after electrochemical lithium intercalation, time in figure indicates the etching duration.

signal peak at 530.1 eV remained fairly constant. Based upon binding energies as reported in the literature [21], we assign the peak at 533 eV to Li₂CO₃, which is expected to result from the exposure of LiOH to air and the second peak at 530.1 eV to MnO₂, present in the material itself.

Fig. 8 shows the XPS spectra of C 1s for the cathode material (γ-MnO₂) after discharge. Two types of carbon peaks were observed, one at 285 eV that we assign to the hydrocarbons present in the electrode material, and the other at 291 eV can be assigned to carbon associated with Li₂CO₃. The intensity of the peak at 285.0 eV, which had a very weak signal before argon ion bombardment, increased in intensity on continuous etching of the overlayer. The other peak at 291 eV in Fig. 7 corresponding to Li₂CO₃ is formed and then removed upon etching indicating that insoluble Li₂CO₃ forms a barrier to H₂O. This is consistent with the change in the O 1s as discussed above for Fig. 7.

Fig. 9 focuses on the region where Li 1s and Mn 3s are expected to occur. It can be seen that the peak at 55.6 eV, which was assigned to the presence of Li₂CO₃ in the unetched material, decreased in intensity on etching. The prolonged etching showed the emergence of another peak at 56.3 eV. This peak is assigned to the underlying lithium intercalated within manganese dioxide, LiₓMnO₂. The basis of this assignment is that the Li species is such that the binding energy of the 1s electron is greater than that of Li in Li₂CO₃. This is likely to be the case with the Li⁺ ion intercalated into the highly oxidizing environment of the MnO₂ structure. The signal at 48 eV, which was barely visible in the unetched material, increased in intensity as the etching period increased. This signal is quite pronounced after 3 h of etching and clearly indicates the presence of Mn, as seen in Fig. 9.

Fig. 10 shows the XPS spectra of Mn 2p. As was observed for the Mn 3s signal, prolonged argon gas etching (3 h) also resulted in increased intensity of the Mn 2p₃/₂ and 3/₂ spin orbit split components. Thus, removal of the outer layer by argon ion etching assists in exposing the true discharge products of the cathode material in saturated LiOH
electrolyte. From the evidence based on the XRD and XPS studies, it can be concluded that lithium is indeed intercalated electrochemically into the host framework of $\gamma$-MnO$_2$ when aqueous LiOH is the electrolyte.

5. Conclusion

The charge–discharge cycle behavior of a novel Zn–MnO$_2$ alkaline battery containing aqueous LiOH electrolyte has been investigated. It is found that the battery with aqueous LiOH electrolyte functions quite differently from the traditional battery, which uses aqueous KOH. When the battery is discharged in cells containing aqueous LiOH, lithium is intercalated into the host framework structure of the positive electrode material, manganese dioxide ($\gamma$-MnO$_2$). The formation of this material is confirmed through XRD and XPS studies of the positive electrode material ($\gamma$-MnO$_2$) before and after discharge and upon subsequent charge/discharge cycling. The mechanism of discharge of $\gamma$-MnO$_2$ differs from the usual products MnOOH, Mn$_2$O$_3$ or Mn$_3$O$_4$, which are formed when KOH is the electrolyte. The LiOH based battery can be reversibly charged. Under the investigated conditions, 56% (162 mAh/g) of the theoretical capacity of the positive electrode active material ($\gamma$-MnO$_2$) to 1 V cutoff voltage could be achieved. The voltaic efficiency is found to be 83% when the battery is charged and discharged at 0.5 mA/cm$^2$ of current density.

Acknowledgements

One of us (M. Minakshi) is particularly grateful to Murdoch University for a research scholarship.

References

Short communication

Lithium insertion into manganese dioxide electrode in MnO$_2$/Zn aqueous battery\textsuperscript{☆}

Part II. Comparison of the behavior of EMD and battery grade MnO$_2$ in Zn|MnO$_2$|aqueous LiOH electrolyte

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Received 5 June 2004; accepted 29 June 2004

Available online 23 August 2004

Abstract

A comparative study of the cathodic behavior of electrolytic manganese dioxide (EMD) and chemically prepared battery grade manganese dioxide (BGM) in Zn|MnO$_2$|aqueous lithium hydroxide (LiOH) cells has been carried out. The X-ray diffraction (XRD), infrared spectra (IR), thermo gravimetric analysis (TGA) and scanning electron microscope (SEM) investigations showed that the two materials had different phase compositions, water content and particle sizes. The cells with BGM had a higher open circuit voltage (OCV) and discharged at higher voltages as compared to those with EMD. The discharge capacity of BGM was lower compared to that of EMD. On discharge both the materials produced same phase i.e. lithium intercalated manganese dioxide (Li,MnO$_2$). This was also confirmed through X-ray photoelectron spectroscopy (XPS) investigation of the discharged products.

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Keywords: Lithium insertion; Battery behavior; Comparison

1. Introduction

The alkaline manganese dioxide battery has advanced to a dominant position in the primary battery market since its introduction in 1960's [1]. γ-Manganese dioxide is a low cost, low toxicity material and its electrochemical characteristics make it an excellent material for use as positive electrode in primary and lithium secondary batteries [2]. Based on the method of production, γ-MnO$_2$ can be categorized as natural manganese dioxide (NMD), chemical manganese dioxide (CMD) and electrolytic manganese dioxide (EMD). The γ-MnO$_2$ polymorph does not denote a unique structure but has been suggested to be either a single phase with considerable disorder [3] or a multi-phase assembly [4]. These materials are made up of varying amounts of pyrolusite (β-MnO$_2$) intergrowth (1 × 1 channels) in the ramsdellite (rare MnO$_2$ material) (2 × 1 channels) matrix. The pyrolusite is characterized by the De Wolff disorder and the microutwinning defect [5].

γ-MnO$_2$ is prepared in many different ways. The material produced by electrolytic methods, commonly called as electrolytic manganese dioxide, is the most commonly used form of MnO$_2$ in batteries. Other forms are also used in batteries but they behave differently. In our previous publication [6], we have shown that EMD undergoes an intercalation...
type of reaction when electroreduced in presence of aqueous lithium hydroxide (LiOH) electrolyte. In this paper, we report our findings on the chemically prepared battery grade manganese dioxide (BGM). The objective is to compare the two materials and to determine whether the BGM behaved in a manner similar to the EMD.

2. Experimental

The EMD and BGM used in this work were purchased from the Foote mineral company and Sigma Aldrich, respectively. The theoretical maximum deliverable electrochemical capacity per unit weight for a one-electron process for both the materials is calculated to be 289 mAh g⁻¹.

The cell design and experimental details were similar to those reported earlier [6]. For X-ray analysis a Siemens X-ray diffractometer using Philips Co Kα radiation was used. The FTIR spectrum was recorded by using a Nicolet Magna-IR 850 spectrometer. The EMD and BGM were reportedly mixed thoroughly with KBr (spectroscopic grade). The mixtures were examined by transmission mode FTIR spectroscopy. For each sample an average of 16 scans were recorded. The surface analysis of the materials was conducted by using a scanning electron microscope (Philips Analytical XL series 20). Thermo gravimetric analysis (TGA) of the sample was conducted by using a TA instruments (SDT 2960). Kratos Ultra Axis Spectrometer using monochromatic Al Kα (1486.6 eV) radiation was used to analyze the chemical binding energy of the samples. The XPS analysis was carried out at pressures below 1 × 10⁻⁹ hPa.

3. Results and discussion

3.1. Characterization of the MnO₂ materials

The EMD and the BGM were characterized by X-ray diffraction (XRD), infrared (IR) spectra, thermogravimetric analysis and scanning electron microscopy (SEM). Fig. 1(a) and (b) show the differences in the X-ray diffraction patterns of the two MnO₂ materials. The XRD peaks of EMD are broad and poorly defined. This is ascribed to non-periodic intergrowth of pyrolusitie and ramsdellite structural units [7]. The XRD patterns of the battery grade manganese dioxide material (Fig. 1(b)), contains four diffraction peaks with 2θ angles 16.3, 19.7, 29.7 and 31. Different researchers have reported different 2θ values for this material, which is explained in terms of variation of composition of the constituent ramsdellite and pyrolusite phases [7–9]. The diffraction peaks at the 2θ angle of 29.7 can be assigned to presence of OH bonds in the structure and the peak at 31 to β-MnO₂. The remaining peaks at 16.3 and 19.7 are characteristic of the γ-phase MnO₂.

The FTIR spectra of the EMD and BGM are compared in Fig. 2. The spectral features of both are almost iden-

![Fig. 1. X-ray diffraction patterns of (a) EMD and (b) BGM before discharge.](image)

![Fig. 2. FTIR spectra of (a) EMD and (b) BGM. (A) Main MnO₂ octahedral vibration and (B) bonded OH.](image)
3.2. Discharge characteristics of Zn|MnO₂|aqueous LiOH cell

Fig. 5 shows the discharge characteristics of Zn|MnO₂|aqueous LiOH cells containing EMD and the BGM as cathode materials. The OCV of the cell with battery grade MnO₂ is higher and the cell discharges at a higher volt-
age under identical conditions. However, the active material utilization of the BGM is lower than that for EMD material. In contrast to EMD the BGM shows a sharp drop in voltage when the delivered capacity approaches 165 mAh g⁻¹. The EMD does not show such drop up to that point. This is probably related to the difference in the composition of the two MnO₂ materials with respect to ramsdellite and pyrolusite, water content and surface area. The two MnO₂ materials exhibit quite different rechargeability when subjected to continuous discharge/charge cycles. For example, while a 35% drop in the active material utilization occurred at cycle number 2 for the cell containing BGM. For EMD, the same drop occurred at the 20th cycle. Thus the EMD is more stable to discharge/charge cycling.

3.3. Characterization of the discharged MnO₂ material in Zn|MnO₂|aqueous LiOH cells

The materials that were produced on discharge (electroreduction) of EMD and BGM in Zn|MnO₂|aqueous LiOH batteries was characterized by X-ray diffraction investigation. As noted earlier the XRD patterns of the two starting MnO₂ materials are quite different (Fig. 1). However, as can be seen Fig. 6, the two materials on discharge have almost identical XRD patterns. For the EMD material d-spacing of 3.27 Å

Fig. 3. Thermogravimetric analysis of (a) EMD and (b) BGM.

Fig. 4. SEM micrographs of images of (a) EMD and (b) BGM.

Fig. 5. Voltage vs. discharge capacity of Zn|MnO₂|LiOH (sat.), 1 M ZnSO₄ cells (a) EMD and (b) BGM.

Fig. 6. X-ray diffraction patterns of (a) EMD and (b) BGM after discharge.
Fig. 7. XPS spectra of Li (1s) for the discharged (a) EMD and (b) BGM.

(2θ = 31.7) is ascribed to the formation of Li intercalated MnO₂ phase (Li₂MnO₂) [11]. For the BGM, d-spacing of the peak is at 3.32 Å (2θ = 31.2). This difference is to be expected because the two phases could differ in the amount of intercalated lithium.

The XPS spectra of Li (1s) of the two discharged materials (EMD and BGM) are shown in Fig. 7. The peaks are assigned with reference to the values reported in the literature [12,13]. Both the discharged materials show Li (1s) peaks at 54.4 eV, which is attributed to lithium intercalated manganese dioxide (Li₂MnO₂). Thus, both the materials produce the same product on discharge in presence of LiOH.

4. Conclusions

The cathodic behavior of electrolytic manganese dioxide and chemically prepared battery grade manganese dioxide in Zn[MnO₂]aqueous lithium hydroxide (LiOH) is compared. The XRD patterns of the two materials are quite different. The BGM is less crystalline and smaller in particle size compared to EMD. The cells with BGM have higher OCV than those with EMD. The BGM cells discharge at a higher voltage when discharged at the same current density, 0.5 mA cm⁻². Even though, the phase composition of the two starting materials are different on discharge in aqueous LiOH electrolyte both produce the same phase, lithium intercalated manganese dioxide (Li₂MnO₂). As compared to BGM, EMD is more stable to discharge/charge cycling.

Acknowledgements

One of the authors (M. Manickam) is grateful to Murdoch University for research scholarship. The technical support of Doug Clarke, Ken Seymour, Stewart Kelly and Peter Fallon all of Murdoch University is also acknowledged.

References

Short communication

Lithium insertion into manganese dioxide electrode in MnO₂/Zn aqueous battery
Part III. Electrochemical behavior of γ-MnO₂ in aqueous lithium hydroxide electrolyte

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Received 30 January 2005; accepted 11 March 2005
Available online 31 May 2005

Abstract

The electrochemical behavior of γ-MnO₂ in lithium hydroxide (LiOH) and potassium hydroxide (KOH) aqueous media has been studied using slow-scan cyclic voltammetry (25 μV s⁻¹) in conjunction with X-ray analysis (XRD) and scanning electron microscopy (SEM). The reduction of γ-MnO₂ in aqueous LiOH results in intercalation of Li⁺ forming a new phase of lithium intercalated MnO₂ (LiₓMnO₂). The process is found to be reversible. In this regard, the reduction of γ-MnO₂ in LiOH is quite different from that in aqueous KOH, which is irreversible and no lithium intercalation occurs. This difference in behavior is explained in terms of the relative ionic sizes of Li⁺ and K⁺. The LiₓMnO₂ lattice is stable only for Li⁺ because Li⁺ and Mn⁴⁺ are of approximately the same size whereas KₓMnO₂ is not stable because K⁺ has almost double the size.

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Keywords: Cyclic voltammetry (CV); γ-MnO₂; Lithium insertion; Rechargeability; Ionic size; Aquous battery

1. Introduction

Manganese dioxide (MnO₂) is commonly used as a cathode in aqueous zinc/MnO₂ batteries, which use KOH as the electrolyte. MnO₂ undergoes reduction through a mechanism involving proton insertion into the MnO₂ structure. In a recent paper [1], we reported that when MnO₂ is discharged in cells containing aqueous LiOH electrolyte the mechanism is quite different, i.e. instead of H⁺ insertion Li⁺ intercalation into the lattice of the host γ-MnO₂ occurs. This intercalation was shown to be reversible. This finding is interesting because it opens up a new field of aqueous batteries utilizing rechargeable γ-MnO₂ cathode.

In this paper, we report the results of a subsequent study, specifically focusing on the mechanism of the intercalation reaction. A cyclic voltammetric (CV) study together with characterization by specialist techniques like X-ray diffraction (XRD) and scanning electron microscope (SEM) of the materials that are formed during the electrochemical discharge of γ-MnO₂ is carried out.

2. Experimental

The cell design, experiment details, and the method of preparing X-ray. XPS and IR samples have been described elsewhere [1,2].

2.1. Slow-scan cyclic voltammetry

For cyclic voltammetric experiments, a three-electrode cell was used. The working electrode, consisted of a disk
(12 mm diameter with 1 mm thickness), γ-MnO₂ mixed with conductive carbon (A-99, Asbury, USA). This disk was embedded into a Pt gauze through which the electric contact was made. The counter electrode was a Zn foil, which was separated from the main electrolyte by means of a porous frit. A saturated calomel electrode (SCE) served as the reference electrode. The electrolyte was a saturated solution of lithium hydroxide. The working electrode was cycled between 0.4 and −0.6 V at 25 μV s⁻¹ scan rate. On each occasion the potential scan started at 0.4 V, moving initially in the cathode direction. At appropriate points of the experiment, the cathode material was removed from the solution, washed with water and characterized by XRD and SEM analysis. All the cyclic voltammetric experiments were done by using EG&G Princeton Applied Research Potentiostat/Galvanostat model 273A, operated by model 270 software (EG&G). All potentials were measured with respect to a saturated calomel electrode. All the electrochemical measurements were carried out at ambient room atmosphere (25 ± 1 °C).

The products formed during the cathodic scan were characterized by X-ray diffraction and scanning electron microscopy. For X-ray analysis a Siemens X-ray diffractometer using Philips Co Kα radiation was used. A (Philips Analytical XL series 20) scanning electron microscope was used for surface analysis investigations.

3. Results and discussion

Fig. 1 shows the first cyclic voltammogram of γ-MnO₂ under the conditions noted in the figure. As can be seen in Fig. 1, the CV profile consists of a reduction peak C₁ at −480 mV and its corresponding anodic peak A₁ at −160 mV. A small shoulder at 46 mV is also seen during the scan in the anodic direction.

Fig. 2 shows the changes in the CV profile when the material is subjected to continuous cycling (20 cycles) in the potential region +0.4 to −0.6 V. The cathodic and anodic peak currents decreased slightly up to about 10 cycles and then tended to stabilize suggesting that the material could be reversibly reduced/oxidized over a number of cycles. To confirm that the anodic peak corresponded to the reduction reaction at −480 mV, the following experiment was done. The γ-MnO₂ was scanned cathodically up to −480 mV and then held constant at that point over 20, 40 and 60 min. At the end of the holding potential, the scan was reversed and the anodic peak current measured. The data is shown in Fig. 3. Clearly, as the time for which the electrode is held at constant potential (−480 mV) the corresponding anodic peak current increases. This observation confirms that the electro reduction of γ-MnO₂ was reversible. The ratio of the charge under the peaks C₁ and A₁ is 0.81 suggesting that the reaction is 81% reversible.

There is a substantial body of literature [3–6] relating to performance characteristics of MnO₂ in alkaline aqueous
MnO$_2$ cells containing potassium hydroxide (KOH) as the electrolyte. The behavior of the MnO$_2$ in aqueous LiOH can be compared to KOH by referring Fig. 4. The data for both the electrolyte were obtained under identical conditions. The CVs of MnO$_2$ in the two electrolytes are quite different. While, the reduction peak in KOH occurs at $-584$ mV, the cathodic peak in the presence of LiOH is at $-480$ mV. Based upon what is known in literature, for KOH electrolyte the cathodic peak has been assigned to the formation of Mn(OH)$_2$ [6,7] and the corresponding anodic peak at $-138$ mV to the oxidation of Mn(OH)$_2$ to a variety of Mn$^{3+}$ intermediates, including $\gamma$-Mn$_3$O$_4$, $\gamma$-MnOOH and $\beta$-MnOOH [6-8]. The reduction/oxidation processes for MnO$_2$ in aqueous KOH are not reversible, and hence the MnO$_2$/KOH system could only be used for non-rechargeable batteries. For LiOH electrolyte, we have assigned the peak at $-480$ mV to the formation of lithium intercalated Li$_x$MnO$_2$ phase and the corresponding anodic peak is reverse of this reaction. As noted earlier MnO$_2$ in aqueous LiOH can withstand repeated reduction/oxidation (Fig. 2) and hence has the potential for being used as a cathode material in rechargeable batteries.

In order to determine the products formed during reduction of MnO$_2$ in both LiOH and KOH electrolyte, the products were characterized by XRD and SEM analysis. The data is shown in Figs. 5–9. Fig. 5 compares the XRD patterns of the $\gamma$-MnO$_2$ before reduction Fig. 5a, and of the material formed on its reduction in LiOH (Fig. 5b) and in KOH (Fig. 5c). The material before reduction showed diffraction lines, characteristic of $\gamma$-MnO$_2$ at the $2\theta$ angle of 16.3, 19.7 and 29.7. A small peak at 31 which is characteristic of diffraction line for $\beta$-MnO$_2$ [9] is also seen indicating that the materials contained some contamination of $\beta$-MnO$_2$ phase. As can be seen in Fig. 5b, the reduction of $\gamma$-MnO$_2$ in LiOH resulted in elimination of the $\gamma$-MnO$_2$ diffraction pattern ($2\theta = 16.3, 19.7$ and 29.7). Only one peak at $2\theta = 31.2$ emerged. Thus, it could be concluded from these results that the discharge process completely changed the structure of the starting $\gamma$-

Fig. 5. X-ray diffraction patterns changes of $\gamma$-MnO$_2$ after the cyclic voltammetry studies in an aqueous battery (a) $\gamma$-MnO$_2$ (before discharge), (b) reduced at $-480$ mV in LiOH media and (c) reduced at $-584$ mV in KOH media.

MnO$_2$ material. The peak at 3.32 Å could be assigned to lithium intercalated (Li$_x$MnO$_2$) material. This is similar to that reported for $\gamma$-MnO$_2$ in non-aqueous lithium cells by Aurbach and co-workers [10]. However, in the case of KOH electrolyte, Fig. 5c, all the characteristic peaks for $\gamma$-MnO$_2$ remained unchanged except for a slight shift to lower $2\theta$ values. Cedar and co-workers [11] have explained this in terms of the difference in the ionic size of the Li$^+$ and K$^+$ ions. As can be seen in Fig. 6, the $\gamma$-MnO$_2$ is an inter growth of ramsdellite (R) and pyrolusite (P). The Mn(IV)O$_4$ octahedra of ramsdellite are linked into double chains, each of which consists of two adjacent single chains that share ocataledral edges [10,11]. These double chains having tunnels with rectangular-shaped cross sections accept the A$^+$ ($A = Li$)

Fig. 6. Schematic diagram of the (a) pyrolusite, (b) ramsdellite and (c) $\gamma$-MnO$_2$, an inter growth between ramsdellite (R) and pyrolusite (P) shown in (001) plane.
cation, which is approximately the same size as that of Mn, the columbic interactions dominate and hence the structure is stable for insertion/extraction of lithium ions. However, the size of the $K^+$ ion is twice as that of $Li^+$; therefore, the insertion site in Fig. 6 is not stable as the electrostatic energy of the structure is diminished. Hence, unlike for $Li^+$ the intercalation of $K^+$ is not possible in the $\gamma$-MnO$_2$ structure.

The surface morphologies of the materials formed during reduction and oxidation of $\gamma$-MnO$_2$ in LiOH and KOH electrolytes were determined by scanning electron microscopy. The SEM micrograph of the $\gamma$-MnO$_2$ before subjecting to reduction/oxidation is shown in Fig. 7. As can be seen from this micrograph, the material was crystalline of particle size 20–25 $\mu$m. The new phase (Li$_x$MnO$_2$), which was formed on reduction, Fig. 8a, had a much finer particle size (5–7 $\mu$m) compared to the original material. The subsequent oxidation of the reduced material produced a phase (Fig. 8b) whose characteristics were quite similar to that of the original $\gamma$-MnO$_2$ (Fig. 7). This particle size was 15–20 $\mu$m. Thus, the reduction/oxidation was almost reversible. This contrast with the material formed after reduction/oxidation cycle of $\gamma$-
MnO₂ in KOH (Fig. 9a and b). As can be seen in KOH the γ-MnO₂ underwent an irreversible change during the cycle.

4. Conclusions

Cyclic voltammetry coupled with X-ray diffraction and scanning electron microscope has been used to investigate structural changes that occur when manganese dioxide is electroreduced and subsequently oxidized. It is found that the reduction of γ-MnO₂ in LiOH produces a new phase of Li₂MnO₂, which is reversible. This differs from the mechanism reported in the literature for reduction/oxidation of the same material in aqueous KOH electrolyte. The difference in the mechanism through which reduction/oxidation of MnO₂ occurs can be explained in terms of the relative ionic sizes of Li⁺ and K⁺ ions. The Li⁺ ions being comparable in size to Mn⁴⁺ could be intercalated into the octahedral structure of γ-MnO₂.

Acknowledgements

One of the authors (M. Minakshi) is grateful to Murdoch University for a research scholarship. The financial support of Australian Institute of Nuclear Science and Engineering (AINSE) to carry out some work at Australian Nuclear Science and Technology Organization (ANSTO) is also acknowledged. The author (M. Minakshi) would like to thank Ken Seymour, Stewart Kelly and Peter Fallon, all of Murdoch University for their technical support in carrying out some of the experiments.

References

Short communication

Redox behavior and surface characterization of LiFePO₄ in lithium hydroxide electrolyte

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Received 27 July 2005; accepted 11 August 2005
Available online 22 November 2005

Abstract

The redox behavior and surface characterization of LiFePO₄ in aqueous lithium hydroxide (LiOH) electrolyte have been investigated. The objective of this work is to investigate the electrochemical behavior of LiFePO₄ in an aqueous lithium hydroxide electrolyte and its comparison with that in non-aqueous lithium ion electrolytes. Cyclic voltammetry results show that LiFePO₄ undergoes partially reversible oxidation/reduction. The products formed on electrooxidation and subsequent reduction of LiFePO₄ were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). It is found that lithium extraction from LiFePO₄ occurs during oxidation. The products formed on subsequent reduction consist of LiFePO₄ and Fe₂O₃.

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Keywords: Redox; Intercalation; Lithium iron phosphate; Lithium hydroxide

1. Introduction

Lithium iron phosphate (LiFePO₄) with an ordered olivine structure has been proposed to be a potential candidate for use as a cathode in non-aqueous electrolyte lithium batteries [1–5]. It is not only cheaper but also less toxic and has higher energy density compared to other phosphate based olivine compounds e.g. LiCoPO₄, LiNiPO₄ or LiMnPO₄. The electrochemical behavior of LiFePO₄ in lithium non-aqueous lithium electrolytes is widely reported in the literature [1–5]. In this media, the electrochemical reaction of LiFePO₄ is generally represented as

LiFePO₄ ⇌ FePO₄ + Li⁺ + e⁻  (1)

Reversible Li⁺ ion extraction/insertion (intercalation) occurs on oxidation/reduction of LiFePO₄. We have carried out a study of the electrochemistry and its surface characterization of LiFePO₄ in aqueous lithium hydroxide electrolyte with metallic zinc as the counter electrode. In this paper, we report our investigation of the reduction/oxidation (redox) behavior of LiFePO₄ in an aqueous lithium hydroxide electrolyte and its comparison with that in non-aqueous lithium ion electrolytes. This work follows on to our recent study of MnO₂ [6,7] where we reported that MnO₂ in aqueous lithium electrolytes behaved quite similar to MnO₂ in non-aqueous electrolytes. To the best of our knowledge there is no reported literature on investigations of LiFePO₄ in aqueous systems.

2. Experimental

The material LiFePO₄ (5 wt.% carbon included) was received from University of Wollongong (UW). Analytical grade Zn foil (99.9%) from BDH Chemicals, reagent grade ZnSO₄·7H₂O from Ajax Chemicals and reagent grade LiOH·H₂O from Sigma Chemicals Company were used as received.

For the cyclic voltammetric studies a standard three-electrode system [6,7] was used. The LiFePO₄ working electrode was made by pressing LiFePO₄ powder onto a disc of Pt gauze. On the other side of the disc, a layer of carbon was also pressed. The disc was inserted into a Teflon barrel. Another Pt disc was inserted into the barrel on top of the carbon side and electrical contact was made by means of a stainless steel plunger. The LiFePO₄ was exposed to the electrolyte through a hole in the Teflon barrel as reported in our previous publications [6,7]. The counter electrode was a zinc foil, which was separated from the

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doi:10.1016/j.powsour.2005.08.059
main electrolyte by means of a porous frit. A saturated calomel electrode (SCE) served as the reference electrode. The recorded values are reported as such. The electrolyte was a saturated aqueous solution of lithium hydroxide. The working electrode was cycled between −0.65 and 0.1 V, each time starting at −0.65 V, going initially in the anodic direction.

An EG&G PAR Potentiostat/Galvanostat model 273A, operated by model 270 software (EG&G) was used to scan the potential at 25 μV s⁻¹ in all experiments. All electrochemical measurements were carried out at ambient room atmosphere (25 ± 1 °C). The products formed during the oxidation/reduction were characterized by a Siemens X-ray diffractometer using Philips Co Kα radiation. X-ray photoelectron spectroscopy (Kratos Ultra Axis Spectrometer) using monochromatic Al Kα (1486.6 eV) radiation was used to analyze the chemical binding energy of the samples. The 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. Secondary ion mass spectrometry (SIMS) spectra were collected on a Cameca ims 5f instrument at the Australian Nuclear Science and Technology Organization (ANSTO), Lucas Heights, Sydney. An O₂⁺ primary ion source (12.5 kV) was used to generate secondary ions. A primary beam of 50 nA was rastered over an area of 250 μm × 250 μm in all experiments. The SIMS negative ion signals corresponding to Li⁺ and Fe⁺ were recorded. An energy offset of −350 V was used to suppress molecular interferences on the peaks of interest.

3. Results and discussion

The X-ray diffraction spectra of the LiFePO₄ material is shown in Fig. 1. The spectra is similar to that reported by Bewlay et al. [8]. This confirms that the material was crystalline of orthorhombic structure.

Fig. 2 shows a typical cyclic voltammogram (CV) of LiFePO₄. The scan was initiated at −630 mV going in the anodic direction to +100 mV and then reversing the scan back to the starting potential. As can be seen, an oxidation peak A₁ at −42 mV occurs during the anodic going portion of the CV. Two cathodic peaks C₁ (−490 mV) and C₂ (−370 mV) are observed during the reverse scan. Two observations can be made from Fig. 2:

(a) The material undergoes oxidation at −42 mV.
(b) Two separate reduction processes occurs during the reverse cathodic scan.

In another experiment (not shown here) the scan was initiated in the same way as before but was held constant for 30 and 60 min at the anodic limit (−42 mV) before reversing the scan. It was found that the peak heights of both C₁ and C₂ increased with the length of time for which the electrode was held at −42 mV. This confirms the cathodic peak (C₁ and C₂) corresponded to the oxidation reaction occurring at −42 mV. The cathode material utilization of LiFePO₄ in aqueous solutions with zinc metal as the anode was found to be 41% (70 mA h g⁻¹) for the first cycle with a voltage profile of 0.8 V [9]. The utilization dropped to 30% (50 mA h g⁻¹) and 20% (40 mA h g⁻¹) for the second and fifth cycles, respectively.

X-ray diffraction spectra of the starting material LiFePO₄ before oxidation and those of the product formed on its electrooxidation together with that of the material formed on subsequent electroreduction are shown in Fig. 3. The X-ray diffraction pattern of LiFePO₄ before oxidation (Fig. 3a) consists of peaks at 2θ = 35.3°, 38.19°, 42.16°, 43.25°, 44.87° and 47.05°. This data matches that reported in the literature for LiFePO₄ [1,8]. The spectra of the material formed on its electrooxidation (Fig. 3b) consists of peaks at 2θ = 35.52°, 38.47°, 42.45°, 43.57°, 45.16° and 47.41°. This data matches that of FePO₄ reported in the literature [1]. These results indicate that FePO₄ is formed on oxidation of LiFePO₄. Thus the oxidation of LiFePO₄ in aqueous LiOH involves de-intercalation of Li⁺ and hence the mechanism resembles that in non-aqueous solvents reported by Padhi et al. [1].
The spectra of the material formed on subsequent reduction of the oxidized product (Fig. 3c) consists of peaks at $2\theta = 35.02^\circ$, $37.95^\circ$, $41.93^\circ$, $43.10^\circ$, $44.65^\circ$ and $46.95^\circ$. This data is again similar to that reported by Padhi et al. in non-aqueous media, who related this to the reversibility of lithium extraction and insertion process. Thus, LiFePO$_4$ in aqueous LiOH media behaves almost identical to that in non-aqueous media. A careful examination of Fig. 3c indicates that there is evidence of the presence of peaks e.g. $2\theta = 35.02^\circ$, which could be assigned to Fe$_2$O$_3$. Thus, the oxidation of LiFePO$_4$ to FePO$_4$ is not fully reversible. Subsequent reduction of the oxidation product of LiFePO$_4$ produces a mixture of LiFePO$_4$ and Fe$_3$O$_4$.

Fig. 4 shows the X-ray photoelectron spectra of the Li (1s) region of LiFePO$_4$ before and after oxidation. For the sample before the oxidation (Fig. 4a) a peak at 55.3 eV corresponding to Li (1s) with a high intensity is seen. The peak at 55.3 eV for the oxidized sample (Fig. 4b) appears as a shoulder with much reduced intensity. This confirms that Li$^+$ is extracted from LiFePO$_4$ during oxidation. Fig. 5 shows the XPS spectra of the Fe (2p) region of LiFePO$_4$ before and after oxidation. The Fe 2p with spin–orbit splitting component of 2p$_{3/2}$ at 710.6 eV and 2p$_{1/2}$ at 724 eV can be seen in the figure. After oxidation a chemical shift of 1.2 eV for Fe 2p$_{3/2}$ is observed even though the 2p$_{1/2}$ does not show any shift. The chemical shift towards higher binding energy can be attributed to the oxidation of Fe(II) to Fe(III) [10].

Further confirmation of extraction/insertion processes of Li$^+$ during oxidation/reduction of LiFePO$_4$ comes from the data shown in Fig. 6. This figure shows changes in the Li/Fe ratio as obtained by secondary ion mass spectroscopic analysis of the products formed on oxidation/reduction of LiFePO$_4$. The data clearly shows that Li/Fe ratio decreases during oxidation and then increases slightly during the reverse process. Based upon the results discussed it can be concluded that LiFePO$_4$ undergoes partially reversible oxidation/reduction via lithium extraction/insertion (intercalation) mechanism in a manner similar to that reported for LiFePO$_4$ in non-aqueous media.
4. Conclusions

The electrochemical oxidation of LiFePO₄ in a saturated aqueous lithium hydroxide (LiOH) electrolyte occurs via lithium extraction mechanism forming FePO₄ similar to that known for non-aqueous media. The reverse reduction of FePO₄ however is not fully reversible as it forms a mixture of LiFePO₄ and Fe₃O₄. In this regard, LiFePO₄ behaved slightly different from MnO₂ and TiO₂ for which we previously reported to undergo reversible lithium intercalation during reduction/oxidation in aqueous LiOH electrolyte. However, if the characterization of the material and the cycling efficiency could be improved then LiFePO₄ can be used as a cathode in a 1 V battery using lithium hydroxide as the electrolyte. The conclusions are confirmed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS).

Acknowledgements

We gratefully acknowledge Prof. S.X. Dou of University of Wollongong for providing a sample of LiFePO₄. One of us (Minakshi Manickam) is particularly grateful to Murdoch University for a research scholarship. The financial support of Australian Institute of Nuclear Science and Engineering (AINSE) for carrying out a part of the work at Australian Nuclear Science and Technology Organization (ANSTO) is also acknowledged.

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M. Minakshi, P. Singh, T.B. Issa, S. Thurgate, R. De Marco, J. Power Sources, in press.
Electrochemical behavior of LiFePO₄ in aqueous lithium hydroxide electrolyte

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Keywords: Iron phosphate, aqueous solutions, lithium insertion, oxidation, reduction, electrochemistry, and olivine.

ABSTRACT

The electrochemistry of olivine-type iron phosphate (FePO₄) as a battery cathode material, in aqueous lithium hydroxide (LiOH), has been investigated. The material forms intercalated LiFePO₄ reversibly on electroreduction/oxidation. The formation of Feₒ₄ phase, in addition to the regeneration of FePO₄ during reverse oxidation of LiFePO₄, also occurs. In this regard, the mechanism of FePO₄ discharge/charge in aqueous LiOH differs from that in non-aqueous solvents.

INTRODUCTION

New olivine-type phosphate-based materials have generated considerable interest as a new class of cathode materials for non-aqueous electrolyte lithium-ion rechargeable batteries. In particular, iron phosphate which has a high voltage and is also eco-friendly has been investigated for use in non-aqueous lithium batteries for electric vehicles [1]. The electrochemical behavior of this material in aqueous media has not been reported in the literature. In this paper, we report the results of our study on its electrochemical behavior in saturated aqueous LiOH electrolyte.

Experimental

LiFePO₄ (including 5 wt. % of carbon) and FePO₄ (amorphous) were provided from University of Wollongong and Kyushu University, respectively. Analytical grade Zn foil (99.9%) from BDH chemicals, reagent grade zinc sulphate Heptahydrate (ZnSO₄.7H₂O) from Ajax chemicals, and reagent grade lithium hydroxide monohydrate (LiOH.H₂O) from Sigma Chemicals Company were used as supplied by the manufacturers.

The experimental procedures for the cyclic voltammetric studies were similar to those reported earlier [2]. The potentials were measured against a standard calomel reference electrode and values reported as such. An EG&G PAR Potentiostat/Galvanostat model 273A, operated by model 270 software (EG&G) was used to scan the potential at 25 µV/s in all experiments. For X-ray analysis a Siemens X-ray diffractometer using Philips Co-Kα radiation was used. The surface analysis of the materials was conducted by using a scanning electron microscope (SEM, Philips Analytical XL series 20).

Results and Discussion

Figure 1 shows the galvanostatic discharge profile of a Zn // FePO₄ cell containing saturated aqueous LiOH and 1 mol.l⁻¹ of ZnSO₄ as the electrolyte. The discharge voltage started at 1.4 V which gradually decreased to 1.0 V followed by a sharp drop. The realizable capacity of the material is calculated to be approximately 70 mAh/g. Figure 2 shows the cyclic voltammogram (CV) of the material when cycled between 0.1 to -0.6 V going first in the cathodic direction. The first cycle consists of a cathodic peak C₁ at - 528 mV and an anodic peak A₁ at - 84 mV.
Fig. 1 The first galvanostatic (0.25 mA/cm²) discharge profile of a Zn | FePO₄ cell containing saturated aqueous LiOH and 1 mol.l⁻¹ of ZnSO₄ as the electrolyte.

Fig. 2 Cyclic voltammogram of FePO₄ in saturated aqueous LiOH (scan rate: 25μv.s⁻¹; potential limit: 0.1 to -0.6 V)

The X-ray diffraction spectra of the FePO₄ before and after the cyclic voltammetric experiment are shown in Fig. 3. The XRD data shows that the material FePO₄ before being subjected to cyclic voltammetry was amorphous and the spectra of the same material after electroreduction (fig. 3b) during the cyclic voltammetric experiment was crystalline. This phase is identified to be LiFePO₄ which is identical to what is reported to be formed when this material is electro-reduced in non-aqueous media. Thus the electroreduction of FePO₄ in LiOH media yields the same product as that reported in non-aqueous media [3]. The reduction of FePO₄ in presence of lithium hydroxide involves an intercalation mechanism, represented by eq. 1.

\[
\text{FePO}_4 + \text{Li}^+ + e^- \rightarrow \text{LiFePO}_4
\]

Eq. [1]

The general characteristics of the XRD spectrum of the material formed on re-oxidation of the electroreduced material (fig. 3c) were similar to those in fig. 3(a). This suggests that the intercalation process was reversible. However, a presence of an additional phase corresponding to Fe₃O₄ is also detected in this spectrum (fig. 3c). The formation of Fe₃O₄ in non-aqueous media is not known. Thus, FePO₄ behaves somewhat differently in aqueous media where a mixture of phases is formed when LiFePO₄ is electroreduced.
Fig. 3 X-ray diffraction pattern of FePO₄ (a) before any electrochemical treatment (b) after electroreduction and (c) after subsequent electrooxidation.

The reduction/oxidation mechanism of FePO₄ was further investigated by subjecting synthetically prepared LiFePO₄ to oxidation followed by reduction through a cyclic voltammetric experiment. The results are shown in Fig. 4. The CV scan started at -630 mV going first in the anodic direction and then reversing it at 100 mV, to a cut-off voltage -630 mV. An oxidation peak A₁ at -80 mV indicates the production of LiFePO₄. A reduction peaks C₁ and C₂ at - 525 and - 405 mV indicates the presence of LiFePO₄ and Fe₃O₄ respectively. This assignment is based upon XRD data of those materials reported in the literature [2]. These result confirm the earlier conclusion that electroreduction of FePO₄ in aqueous media is similar to that in non-aqueous media. However, the mechanism of reverse oxidation is quite different.

Fig. 4 Cyclic voltammogram of LiFePO₄ in saturated aqueous LiOH (scan rate: 25μV.s⁻¹; potential limit:−0.6 V to 0.1).

The change in the surface morphology of the materials formed during reduction and re-oxidation of FePO₄ can be seen from the SEM micrographs in Fig. 5. The results show that original material, FePO₄, (fig.5a) before electroreduction was amorphous of particle size 25-30 μm. The product formed during reduction, LiFePO₄ (Fig. 5b), was crystalline with very fine particle size 10-12 μm. The product formed on subsequent oxidation (fig. 5c) had morphology very different from that shown in figs. 5(a) and (b). The particle size of the material was even finer (< 5μm) is lower than that of the original material and that of the electroreduced material.
Fig. 5 Scanning electron micrographs of the FePO₄ (a) before any electrochemical treatment (b) after electro reduction and (c) after subsequent electro oxidation.

Conclusions
It is concluded that the reduction of FePO₄ results in the formation of intercalated FePO₄. Subsequent oxidation of this material generates two phases consisting of FePO₄ and Fe₃O₄. In this regard, FePO₄ behaves quite differently in aqueous media compared to what is reported for the same in non-aqueous media.

Acknowledgements
We gratefully acknowledge Prof. S. Okada of Kyushu University for providing a FePO₄ sample. One of us (M.M.) is grateful to Murdoch University for a research Scholarship. The financial support of Australian Nuclear Science and Engineering (ANSE) for carrying out a part of the work at Australian Nuclear Science and Technology organization (ANSTO) is also acknowledged.

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Electrochemical behavior of anatase TiO$_2$ in aqueous lithium hydroxide electrolyte

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Received 24 August 2005; accepted in revised form 14 December 2005

Key words: anatase, LiTiO$_2$, oxidation, reduction, TiO$_2$

Abstract

The electrochemical behavior of titanium dioxide (TiO$_2$) in aqueous lithium hydroxide (LiOH) electrolyte has been investigated. Cyclic voltammetry shows that the electroreduction results in the formation of a number of products. X-ray diffraction of the electroreduced TiO$_2$ shows that Li$_x$TiO$_2$, Ti$_2$O$_3$, Ti$_5$O$_9$ and TiO are formed. The formation of Li$_x$TiO$_2$ is confirmed through X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) studies of the electroreduced TiO$_2$. The formation of Li$_x$TiO$_2$ is electro-reversible. In this respect, the electrochemical behavior of TiO$_2$ in concentrated aqueous lithium hydroxide electrolyte is similar to that for lithium perchlorate (LiClO$_4$) non-aqueous media.

1. Introduction

In recent years much effort has been directed towards the development of renewable energy conversion and storage devices based on inexpensive materials. In this respect titanium dioxide (TiO$_2$) has attracted considerable academic and practical interest. Its semi-conducting properties together with its chemical stability make it an excellent candidate for use in rechargeable batteries, electrochromic devices and solar cells. In particular, it has been extensively used in lithium ion batteries. It is due to its ability to accommodate small foreign ions, such as Li$^+$ and H$^+$ in its host structure through an intercalation process. Titanium dioxide exists in nature in various polymorphs [1] such as rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). The rutile and anatase are the most thermodynamically stable phases and common forms of the TiO$_2$. These materials behave differently when used as cathodes in lithium cells. Ohzuku and Koizumi [2] showed that diffusion of lithium into the TiO$_2$ (anatase) was easier than for rutile, because of different structural features. The electrochemical behavior of anatase TiO$_2$ in lithium ion non-aqueous electrolytes has been widely reported [3–6].

In non-aqueous lithium electrolytes, the following reaction for TiO$_2$ is generally written [2]

$$\Box \text{Ti}^{4+} + x\text{Li}^+ + x\text{e}^- \Leftrightarrow \text{Li}_x\text{Ti}^{4+}_x\Box + \text{O}^{2-}$$  (1)

where $\Box$ denotes vacant sites and $x$ varies from 0.5 to 1, depending on the experimental techniques used.

Very little information on the electrochemical behavior of TiO$_2$ in aqueous media is available. Lyon and Hupp [7, 8] reported that the electrochemical reduction of TiO$_2$ involves irreversible (H$^+$) proton uptake (protonation) in aqueous H$_2$SO$_4$ or NaOH electrolytes. This proton intercalation mechanism was supported by electrochemical quartz crystal microbalance (EQCM) measurements. In this paper, we report our investigation of the reduction/oxidation (redox) behavior of TiO$_2$ (anatase) in an aqueous lithium hydroxide electrolyte and its comparison with that in non-aqueous lithium ion electrolytes. This work follows on our recent study of MnO$_2$ [9–11] where we reported that MnO$_2$ in aqueous lithium electrolytes behaved very similar to that in non-aqueous electrolytes.

2. Experimental

A list of the chemicals used in this study is given in Table 1. A standard three-electrode system was used for the cyclic voltammetric studies as shown in the Figure 1. The TiO$_2$ working electrode was made as follows: TiO$_2$ powder was pressed onto a disc of Pt gauze. On the other side of the disc, a layer of carbon was also pressed. The TiO$_2$ side of the disc (thickness of 1 mm) was exposed to the LiOH electrolyte through a Teflon barrel as shown in Figure 1. For making electrical connection of TiO$_2$ a Pt disc was inserted into the barrel on top of the carbon side which contacted stainless steel plunger. The counter electrode was a Zinc foil, which was separated from the main electrolyte by means of a
Table 1. List of chemicals

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Supplier</th>
<th>Grade (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>Sigma-Aldrich</td>
<td>99.9</td>
</tr>
<tr>
<td>Zn foil</td>
<td>BDH chemicals</td>
<td>99.9</td>
</tr>
<tr>
<td>Lithium hydroxide monohydrate</td>
<td>Sigma chemicals</td>
<td>99.9</td>
</tr>
<tr>
<td>Zinc sulphate heptahydrate</td>
<td>Ajax chemicals</td>
<td>99.9</td>
</tr>
</tbody>
</table>

Fig. 1. Schematic diagram of a three cell system.

The products formed during the electroreduction of TiO₂ were characterized by a Siemens X-ray diffractometer using Philips CoKα radiation. X-ray photoelectron spectroscopy (Kratos Ultra Axis Spectrometer) was used to analyze the chemical binding energy of the samples using monochromatic AIXα (1486.6 eV) radiation. The X-ray photoelectron spectroscopy (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 Fourier transform infrared spectrum (FTIR) was recorded using a Nicolet Magna-IR 850 spectrometer. For the FTIR study, TiO₂ was mixed thoroughly with KBr and for each sample an average of 16 scans were recorded.

3. Results and discussion

3.1. Reduction/oxidation (redox) behavior of anatase TiO₂

The redox behavior of the anatase TiO₂ was investigated voltammetrically by cycling in the potential region 0 to −0.6 V. Figure 2 shows one such cyclic voltammogram (CV). The cathodic portion of the scan consists of a series of peaks. The prominent peaks occur at potentials −396 and −496 mV. The reverse anodic scan consists of only one peak at −200 mV. This suggests that the reduction of TiO₂ occurs through more than one mechanism but only one reduction product undergoes reversible oxidation. The products of electroreduction of TiO₂ were identified by various techniques as discussed in the following section.

3.1.1. X-ray diffraction

Figure 3 shows the X-ray diffraction pattern of the material formed on scanning TiO₂ to −496 mV, the potential where reduction occurs. The X-ray diffraction pattern of the TiO₂ before the reduction experiment (Figure 3a) matches that of anatase TiO₂ having a tetragonal lattice with a = 3.792 Å and c = 9.514 Å. The material formed after the reduction scan (Figure 3b) shows new peaks at 2θ = 36.1°, 37.3°, 39.8°, 41.2° and 52.3° in addition to those present in the original material (Figure 3a). Based on the literature we assign the peak at 2θ = 37.3° to Ti₂O₃ and those at 41.2° and 52.3° to Li₄TiO₅ [2, 12]. The peaks at 2θ = 36.1° and 39.8° are assigned to Ti₅O₈ and TiO, respectively. This indicates that the electroreduction of TiO₂ leads to the formation of intercalated TiO₂ (Li₄TiO₅), Ti₅O₈, Ti₅O₈ and TiO. Since the ionic radius of Li⁺ is almost identical to that of Ti⁴⁺ radii (~0.7 Å) the formation of lithium

![Fig. 2. Cyclic voltammogram of TiO₂ (scan rate: 25 μVs⁻¹).](image)

![Fig. 3. X-ray diffraction patterns of titanium dioxide (TiO₂) (a) before reduction (b) after electroreduction at −496 mV and (c) after subsequent electrooxidation at −200 mV.](image)
intercalated TiO₂ is reasonable. In this regard, the behavior of TiO₂ in aqueous LiOH electrolyte is similar to that in non-aqueous LiClO₄ electrolyte [2, 13–16]. However, the phases Ti₂O₃, TiO and Ti₃O are not seen in the non-aqueous systems, but, Lyon and Hupp [7] explained the formation of these reduced phases in aqueous system via irreversible proton intercalation. The XRD pattern of the material (Figure 3c) formed on subsequent oxidation at −200 mV does not contain the peaks at 41.2° and 52.3° indicating the Li₁₂TiO₂ receptive back to TiO₂. All the other peaks corresponding to TiO₂ remain unchanged. Thus the intercalation of TiO₂ to form Li₂TiO₃ is reversible.

3.1.2. X-ray photoelectron spectroscopy

Figure 4a shows the X-ray photoelectron spectra (XPS) of the TiO₂ before reduction at −496 mV. The symmetric Ti 2p peaks, indicate the material to be stoichiometric TiO₂ with a low concentration of defects. The spin-orbit splitting was 5.6 eV, with an intensity ratio of 0.26 between the Ti 2p₁/₂ and Ti 2p₃/₂. Figure 4b shows Ti (2p) peaks of the same material after electro-reduction at the fifth scan. As can be seen in Figure 4b, a clear chemical shift of Ti (2p) towards lower binding energy is observed. This chemical shift reflects the change of Ti⁴⁺ to Ti³⁺ oxidation state. Ebina et al. [15] and Sodergren et al. [17] also observed a similar chemical shift of Ti (2p) when TiO₂ was electroreduced in non-aqueous LiClO₄ electrolyte indicating the formation of lithium intercalated TiO₂ phase (Li₂TiO₃).

Figure 5 shows the XPS spectra of the Li(1s) region of TiO₂ before and after electroreduction. For the unreduced sample no signal corresponding to Li (1s) is seen (Figure 5a), instead, only a satellite peak of Ti (3s) at 59.5 eV region occurs. The material after reduction (Figure 5b) contains a highly developed peak corresponding to Li (1s) at 55.1 eV [18]. To eliminate the possibility that the observed Li (1s) signal for the electroreduced sample was not just due to some lithium impurity such as Li₂CO₃ which could have been formed through the exposure of the TiO₂ to the electrolyte LiOH and atmospheric CO₂, the following experiment was done. The material after electroreduction was washed thoroughly with acetone several times until no further Li⁺ ions were detected in the washing liquid. The resultant powder was dried and pressed back into a pellet and its XPS spectra recorded. As can be seen from Figure 6, the Li (1s) was still present suggesting that the material indeed was Li₂TiO₃. Chauvat et al. [19] have reported similar XPS data for the formation of Li₂TiO₃ in molten Li₂CO₃–Na₂CO₃ fuel cells.
3.1.3. Infra-red spectra
The infra-red spectra of TiO$_2$ material in the region 500–1000 cm$^{-1}$ is shown in Figure 7. The broad peak at around 700 cm$^{-1}$ for the material before the electroreduction, Figure 7a, corresponds to TiO$_2$ lattice vibration similar to that reported by Lee et al. [20]. The spectra for the same material after electroreduction have a new peak at 600 cm$^{-1}$ (Figure 7b), similar spectra were observed for Li$_2$Ti$_3$O$_7$ by Picquart et al. [21].

4. Conclusions
The electrochemical behavior of TiO$_2$ in a saturated aqueous LiOH electrolyte was investigated. It was found that reduction of TiO$_2$ in aqueous LiOH occurs forming a number of reduction products. Only one of these products can be reversibly oxidized. The X-ray diffraction (XRD) studies show that Li$_3$Ti$_2$O$_5$ is the product which is reversibly formed during electroreduction/oxidation. Additionally, Ti$_2$O$_3$, Ti$_2$O and TiO phases are also formed which are not reversible. X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared (FTIR) spectral studies of the material confirm the formation of lithium intercalated TiO$_2$. This behavior of TiO$_2$ is found to be similar to that reported for lithium perchlorate (LiClO$_4$) non-aqueous electrolytes.

Acknowledgements
One of us (Minakshi Manickam) is grateful to Murdoch University for a research scholarship. The financial support of Australian Institute of Nuclear Science and Engineering (AINSE) to carry out some work at Australian Nuclear Science and Technology Organization (ANSTO) is also acknowledged. M. M thanks Doug Clark, Ken Seymour and Stewart Kelly of Murdoch University for their technical support in carrying out some of the experiments.

References
12. JCPDS cards: 16-223 and 10-63.
Electrochemical Behavior of Olivine-Type LiMnPO₄ in Aqueous Solutions

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The electrochemical behavior of olivine-type lithium manganese phosphate (LiMnPO₄) as a cathode material was investigated in a saturated aqueous lithium hydroxide electrolyte. The crystal structure and surface characterization of the olivine type LiMnPO₄ and the products which are formed on its oxidation and subsequent reduction were studied. X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, and secondary ion mass spectrometry were used for these investigations. LiMnPO₄ was found to be reversibly delithiated/oxidized.

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Manuscript submitted March 28, 2006; revised manuscript received June 6, 2006. Available electronically August 8, 2006.

Among the known Li extraction/insertion (delithiation/lithiation) compounds, the layered oxides LiCoO₂, LiNiO₂, and the spinel LiMn₂O₄ are now commercially used as 4 V positive electrode materials in rechargeable lithium batteries. However, these materials suffer from poor electrochemical stability in their highly oxidized state. In LiMn₂O₄, the reduction of manganese below Mn⁴⁺ leads to a Jahn-Teller distortion. The major problem hindering the development of LiMn₂O₄ as a cathode material is the loss of capacity with extensive cycling. Phosphate-based electrode materials, especially the phospho-olivines LiMPO₄ (where M = Fe, Mn, Co, and Ni) are now recognized as attractive alternatives to oxide materials. The presence of (PO₄)³⁻ polyions with a strong P-O covalent bond in the olivine type structure provides a stable system when the electrode is fully charged. Hence it seems attractive to use phospho-olivines of LiMPO₄ as a cathode material in nonaqueous secondary batteries. Since the pioneering study on LiFePO₄ by Pahde et al., significant efforts have been made on the substitution of Fe with Mn, Co, and Ni and their suitability as cathode materials in lithium batteries. Its electrochemical behavior in nonaqueous solvents has been reported in the literature.

All of the available literature on phospho-olivine electrodes is limited to nonaqueous electrolyte solvents. No studies in aqueous media are known to the best of our knowledge. In a previous paper, we have reported a systematic study of the electrochemistry of LiFePO₄ in aqueous lithium hydroxide electrolyte. The objective was to establish how this material behaved as a cathode material in aqueous media compared to that in nonaqueous electrolytes. The present work follows on our recent study of MnO₂, TiO₂, and LiFePO₄, where we reported that MnO₂ in aqueous lithium electrolyte behaved similar to that in Li⁺ nonaqueous electrolyte and found to be a potential candidate for an aqueous secondary battery system.

This has motivated the search for other potential transition metal olivine like manganese as the substitution, i.e., LiMnPO₄. Hence, in this paper, we extend our study to LiMnPO₄ as a cathode material in aqueous batteries. The redox behavior and the surface characterization of these materials are reported in detail.

Experimental

The LiMnPO₄ (10 wt % carbon included) were received from Tokyo Institute of Technology and its cathode properties are reported in the literature. Analytical grade Zn foil (99.9%) from BDH chemicals, reagent grade LiOH·H₂O from Sigma Chemicals Company, and zinc sulfate heptahydrate (ZnSO₄·7H₂O) from Ajax Chemicals were used as received.

The experimental procedures for the cyclic voltammetric (CV) and galvanostatic studies and its standard cell configuration were similar to those reported earlier. A saturated calomel electrode (SCE) served as the reference electrode. Reported potentials are relative to SCE.

An EG&G PAR potentiostat/galvanostat model 273A, operated by model 270 software (EG&G) was used to scan the potential at 25 μV/s in all experiments. For X-ray analysis a Siemens X-ray diffractometer (XRD) using Philips Co Ka radiation was used. Kras Ultra Axis spectrometer using monochromatic Al Ka (1486.6 eV) radiation was used to analyze the chemical binding energy of the samples. The XPS analysis was started when the pressure in the analysis chamber fell below 1 × 10⁻⁹ kPa. Carbon (C1s), was used as a reference for all the samples. The surface analysis of the materials was conducted by using a scanning electron microscope (SEM, Philips Analytical XL series 20). Secondary ion mass spectrometry (SIMS) spectra were collected on a Cameca ims 5f instrument at the Australian Nuclear Science and Technology Organization (ANSTO), Lucas Heights, Sydney. An O²⁻ primary ion source (12.5 kV) was used to generate secondary ions. A primary beam of 50 nA was rastered over an area of 250 × 250 μm² in all experiments. The SIMS positive ion signals corresponding to ⁷Li was recorded.

Results and Discussion

Electrochemical behavior of LiMnPO₄ in aqueous cell.—Figure 1 shows the XRD profile of LiMnPO₄. The data matched with single-phase orthorhombic (olivine structure) as reported in the literature. Its redox behavior can be seen (Fig. 2) from the CV in the potential region 0.65 to 0.1 V.

The scan was initiated at —360 mV going first in the anodic direction to +100 mV and then reversing the scan back to the starting potential. An oxidation peak A₁ occurs at 65 mV in the anodic going portion of the CV. A cathodic peak C₁ is observed during the

![Figure 1. XRD pattern of the starting material LiMnPO₄ as powder.](image-url)
reverse scan at -480 mV. Thus, the material undergoes electro-oxidation/reduction presumably involving a change of the oxidation state of the Mn atom in LiMnPO₄. The large potential gap between the oxidation and reduction seems to suggest that the electron transfer process is very slow in aqueous solutions.

The characteristics of the Zn[LiOH + ZnSO₄][LiMnPO₄] cell was charged and discharged galvanostatically (0.25 mA/cm²) to 1.9 and 0 V cutoff, respectively. During the charge process a slight inflection around 1.1 and 1.5 V is shown in Fig. 3. This could be due to the twinning effect caused by the delithiation in the olivine structure. However, during the discharge process, no such inflections have been seen in Fig. 3. There was a constant decrease in potential till the discharge cutoff voltage of 0.0 V. Although the shapes of the charge and discharge curve are different the cells could be reversibly charged and discharged in aqueous solutions.

The cathode material utilization versus the cycle number is shown in Fig. 4. The percentage of material utilization during discharge process dropped from 44 to 32% for the first cycle after which it stabilized. At cycle 20, the cathode material utilization for discharge was only 15%. The theoretical maximum electrochemical capacity deliverable per unit weight for a one-electron process is 170 mAh/g.

Characterization of the cathode material.—With the objective of identifying the products formed on electro-oxidation and reverse reduction, the following experiment was done. The material was subjected to electro-oxidation in a three-cell configuration under galvanostatic conditions (0.25 mA/cm²). The products formed were examined by XRD, SEM, XPS, and SIMS. The electro-oxidized material was then subjected to reverse reduction galvanostatically at the same current density. The resulting material was also analyzed by using the same techniques as noted above.

XRD spectra of the starting material LiMnPO₄ before oxidation and after its electro-oxidation are shown in Fig. 5a and b. As can be seen in Fig. 5b, the XRD spectrum of the oxidized material differs significantly from that of the starting material. New reflections at 2θ = 25.1, 30.6, 35.3, and 42.2° are seen. These peaks are in good agreement with those reported for the mineral (ICDD card no: 70-0180) of formula MnPO₄. The XRD pattern of the product formed on electro-oxidation of LiMnPO₄ is indicative of the lower crystallinity of the product which in this case is delithiated MnPO₄. This is also reflected in the SEM of this material as shown in Fig. 6. The product has very different morphology compared to the material before the oxidation (Fig. 6). These results indicate that the phase observed at the end of electrochemical oxidation for LiMnPO₄ is MnPO₄, suggesting lithium is extracted.

Figure 5c shows the XRD pattern of the material formed on reverse reduction of the MnPO₄ formed previously by electro-oxidation of LiMnPO₄. The XRD pattern of this material now matches that of the original raw material which had not been subjected to any electrochemical treatment. It is also in accordance with the comparison of morphology (before oxidation and after reduction) in Fig. 6. This suggests that the electro-oxidation of LiMnPO₄ is reversible via a lithium intercalation, i.e., oxidation of LiMnPO₄ forms MnPO₄ which on subsequent reduction reverts back to LiMnPO₄.
Thus the electro-oxidation/reduction of LiMnPO₄ in aqueous LiOH involves delithiation/lithiation and its mechanism is similar to that in nonaqueous solvents reported by Delacourt et al.¹⁰ and Li et al.¹³

To confirm any presence of lithium ions in the solid matrix of the electro-oxidized/reduced LiMnPO₄ material it was subjected to XPS studies. The cathode material after electrochemical process was covered with a thick layer of lithium carbonate in the sample.¹⁴ Hence, the material was washed¹⁵ thoroughly with acetone and deionized water several times and the resultant powder was mounted for the XPS and SIMS analysis. Figure 7 shows the XPS spectra of the Li (1s) region for the LiMnPO₄ material before electrochemical treatment, after electro-oxidation, and after electroreduction. The peak at 56.4 eV corresponds to the Li 1s.¹⁹ As can be seen from the Fig. 7, the peak intensity at 56.4 eV corresponding to Li (1s) is high in sample (a) and (c) but very low for sample (b). This confirms that on electro-oxidation, Li⁺ is removed from LiMnPO₄ and is reinserted into MnPO₄ after the material has been reduced back. This result provides further evidence to reversible delithiation of LiMnPO₄ on oxidation.

Further confirmation of delithiation/lithiation of Li⁺ during oxidation/reduction of LiMnPO₄ is obtained from the secondary ion mass spectrometry (SIMS) analysis. Figure 8 shows changes in the Li⁺ ion counts as obtained by SIMS analysis of the products formed on oxidation of LiMnPO₄ and its reverse reduction. The data shows that during oxidation the Li⁺ count is decreased and then increases on reverse reduction. This supports the delithiation mechanism for oxidation/reduction of LiMnPO₄.

Based on the results discussed above, it can be concluded that the electrochemical oxidation of LiMnPO₄ leads to the phase MnPO₄ and on subsequent reduction reverts back to LiMnPO₄.

Conclusions

The preliminary electrochemical investigation of lithium manganese phosphate (LiMnPO₄) in aqueous LiOH shows that delithiated MnPO₄ is formed when LiMnPO₄ is electro-oxidized. This process is reversible. This is confirmed by the analysis of the products formed on electro-oxidation/reduction of LiMnPO₄ using XRD, SEM, XPS, and SIMS.

Olive-type LiMnPO₄ showed a reversible redox reaction and behaved in a slightly different way from LiFePO₄, which we previously reported to undergo a partial reduction forming a mixture of LiFePO₄ and Fe₃O₄. However, if the characterization of this material and the cycling efficiency could be improved then LiMnPO₄ can be used as a cathode in a 1 V battery using lithium hydroxide as the electrolyte.

Acknowledgments

We gratefully acknowledge Professor Atsuo Yamada of Tokyo Institute of Technology for providing a LiMnPO₄ sample. M.M. is grateful to Murdoch University for a research scholarship. The financial support of Australian Nuclear Science and Engineering (ANSE) for carrying out a part of the work at Australian Nuclear Science and Technology (ANSTO) is also acknowledged.

Murdoch University assisted in meeting the publication costs of this article.
References

Appendix (B)

Papers published in the proceedings of the conferences
Electrochemical Characterization of $\gamma$-MnO$_2$ in Zn/ MnO$_2$/ LiOH (aqueous) Cells

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Abstract
The mechanism of discharge of $\gamma$-MnO$_2$ [electrolytic manganese dioxide (EMD type)] in Zn/ MnO$_2$/ LiOH (aqueous) cells was investigated. The cells were discharged at 0.5mA/cm$^2$ current density to a cut-off voltage of 1.0 V. The cathode material formed after the discharge was analyzed by X-ray diffraction (XRD), Scanning electron microscopy (SEM), Infrared spectra (IR) and X-ray Photoelectron spectroscopy (XPS) techniques. It is found that during the cell discharge, the electro reduction of $\gamma$-MnO$_2$ occurs via a lithium intercalation process in presence of aqueous saturated LiOH as electrolyte.

Keywords: Aqueous battery, Lithium insertion, XRD.

Introduction
Primary alkaline Zinc-Manganese dioxide dominates the primary battery market. These batteries are based on the electrochemical insertion of protons into $\gamma$-MnO$_2$ during the discharge process [1]. The properties of $\gamma$-MnO$_2$ in relation to its use in these batteries have been studied extensively. Giovanali, Maurer and Feitknecht [2] described $\gamma$-MnO$_2$ as an intergrowth structure between ramsdellite and pyrolysite, which are both members of the rutile group. The basic unit cells are [MnO$_6$]-octahedra joined to form alternating single-and double chains. Other forms of $\gamma$-MnO$_2$ have also been looked at, Ruetschi et al [3] have summarized the types of MnO$_2$ materials which are considered to be important for batteries, among these electrolytically produced manganese dioxide (EMD) is widely used commercially.

In traditional alkaline batteries using KOH as the electrolyte the electro reduction of the cathode material MnO$_2$ during discharge involves insertion of protons into the ionic lattice of the manganese dioxide according to the equation:

$$\text{MnO}_2 + \text{H}^+ + e^- \rightarrow \text{MnO}_2 \cdot \text{H}_2\text{O}$$  \hspace{1cm} [1]

In contrast, we have reported earlier [4] the use of aqueous LiOH as an electrolyte results in the incorporation of lithium ions into the MnO$_2$ structure during the discharge

$$\text{Li}^+ + \text{e}^- + \text{MnO}_2 \rightarrow \text{LiMnO}_2$$  \hspace{1cm} [2]

The overall reaction of the alkaline Zn/MnO$_2$ battery using LiOH electrolyte is:

$$\text{Li}^+ + \text{e}^- + \text{MnO}_2 \rightarrow \text{LiMnO}_2$$  \hspace{1cm} [3]

This reaction is similar to that of Li/MnO$_2$ nonaqueous batteries. During cell discharge, Li$^+$ ions are inserted into the $\gamma$-MnO$_2$ structure, when the oxidation state of Mn (IV) changes to Mn (III). During charge, it reverts to its original phase when removal of Li$^+$ ions from the structure occurs.

This study is an extension of the work, which was reported earlier [4]. The present study focuses on identifying the products, which are formed when $\gamma$-MnO$_2$ is discharged in batteries containing aqueous LiOH to confirm the Li intercalation mechanism that we proposed earlier. The products of discharge were characterized by X-ray diffraction (XRD) and spectroscopic techniques, like X-ray photoelectron spectroscopy (XPS) and Infrared spectra (IR) and also surface analysis technique by Scanning electron microscopy (SEM).

Experimental
The experimental procedures were similar to those reported earlier [4]. For X-ray analysis a Siemens X-ray diffractometer using Philips Co-K$\alpha$ radiation was used. Kratos Ultra Axis Spectrometer using monochromatic Al K$\alpha$ (1486.6 eV) radiation was used to analyze the chemical binding energy of the samples. The XPS analysis was started when the pressure in the analysis chamber fell below 1 x 10$^{-6}$ hPa. The FTIR spectra was recorded by using a Nicolet Magna-IR 850 spectrometer. Samples of the cathode material were thoroughly mixed with KBr (spectroscopic grade) and examined by transmission mode FTIR spectroscopy. For each sample an average of 16 scans were recorded. The surface analysis of the materials was conducted by using a scanning electron microscope (Philips Analytical XL series 20).

Results and Discussion
Performance characteristics of Zn-MnO$_2$ aqueous LiOH cell: The performance characteristics of MnO$_2$ in alkaline aqueous Zn-MnO$_2$ cells containing potassium hydroxide (KOH) as the electrolyte have been reported extensively in the literature [5-7]. Kordesch [7] has reported that the discharge behavior of the cathode material, MnO$_2$ in the alkaline KOH electrolyte occurs in a heterogeneous phase reaction, i.e. MnO$_2$ being converted to Mn$_2$O$_3$. Hence, the MnO$_2$ lattice expands and, at a certain point of discharge, the mechanism changes to an irreversible portion of the MnO$_2$ reduction process. We have investigated the use of LiOH in place of KOH in alkaline Zn - MnO$_2$ cells.
Zn/MnO₂/LiOH (aq.) cells were discharged at constant current density (0.5 mA/cm²) to 1 V cut-off. For comparison, cells containing KOH in place of LiOH were also discharged under identical conditions. Each of the electrolytes contained 1 M ZnSO₄ in addition to the saturated solutions of LiOH or KOH. The results for the first discharge cycle for both the cells are shown in Fig. 1. The cell containing LiOH discharged at a higher voltage and had a higher material utilization compared to the cell with KOH electrolyte. The cathode utilization for the LiOH cell was found to be 56 % (162 mAh/g) as compared to 41 % (120 mAh/g), for the KOH cell.

The reversibility of the Zn-MnO₂ cell with the LiOH electrolyte was investigated. The Fig. 2 shows a typical charge/discharge cycle indicating that the voltaic efficiency was 83%.

The cathode material utilization varied with the cycle number as is shown in Fig. 3. The utilization initially dropped rapidly up to cycle 10 after which it decreased gradually. At the cycle number 40 the utilization was only 16%.

**Characterization of the cathode material:** The characterization of the cathode material which was produced on discharge of the active MnO₂ material was carried out by XRD, XPS, SEM and FTIR techniques. Figures 4 (a) and (b) show the x-ray diffraction patterns of the cathode material γ-MnO₂ before and after discharge. The sample before discharge showed four diffraction lines at the 2θ angle of 16.3, 19.7, 29.7 and 31.2.

**Fig. 1.** First discharge curve of Zn-MnO₂ cells using saturated aqueous of (a) KOH and (b) LiOH each containing 1 mol. L⁻¹ ZnSO₄ under identical conditions.

**Fig. 2.** The first discharge-charge profile of Zn-MnO₂ cells using saturated aqueous LiOH containing 1 mol.L⁻¹ ZnSO₄ as the electrolyte.

**Fig. 3.** The cathode material (γ-MnO₂) utilization in Zn|MnO₂|aqueous LiOH battery versus cycle number.

**Fig. 4.** X-ray diffraction pattern changes of γ-MnO₂ in Zn|MnO₂|aqueous LiOH battery (a) before discharge (b) after discharge to 1.0 V cut off.
lines at 16.3, 19.7 and 29.7 are characteristic peaks for \(\gamma\)-\(\text{Mn}_2\) whereas the line at 31.2 corresponds to \(\beta\)-\(\text{Mn}_2\). As can be seen in Fig. 4(b), after discharge, the peaks responding to the \(\gamma\)-\(\text{Mn}_2\) \((2Q = 16.3, 19.7\) and 29.7) not remaining. The peak at 31.2 shifted slightly to the \(2Q\) diffraction angle \((d\)-spacing of 3.27 Å\) position. It is from these results that the discharge process slightly changes the structure of the starting material. peak at 3.27 Å could be assigned to intercalated \(\gamma\)-\(\beta\)- \(\text{Mn}_2\). This is similar to that reported for non-aqueous \(\text{Li}^+\) cells by Aurbach et al [9].

SEM micrographs of the cathode material before and discharge are shown in Fig. 5. As can be seen from the micrograph, Fig. 5(a), the particle size of the material formed after the discharge was of the order of 20-25 μm. The material formed after the discharge had a very different morphology (Fig. 5b). The particle size was of the order 0 μm. It appears that during discharge the original \(\gamma\)-\(\text{Mn}_2\) particles agglomerate into larger particles perhaps using lithium ions intercalated into the material.

![Image](attachment:image1)

**Fig. 5.** Scanning electron micrographs of \(\gamma\)-\(\text{Mn}_2\) cathode material (a) before discharge and (b) after discharge.

to XPS studies. As reported earlier [4], before the XPS analysis, the surface of the cathode material was ion bombarded to remove the thick layer of materials (like \(\text{LiOH}, \text{Li}_2\text{CO}_3\) and \(\text{H}_2\text{O}\)) on the surface of the discharged products. \(\text{LiOH}\) is present because the material is discharged in \(\text{LiOH}\), which remains adsorbed at the surface. The lithium carbonate is the result of \(\text{LiOH}\) reacting with atmospheric carbon dioxide. After ion bombardment, the spectra shown in Fig. 6 were recorded. The peak at 54.7 eV could be assigned to intercalated lithium [10] into the \(\text{Mn}_2\) host structure.

![Image](attachment:image2)

**Fig. 6.** XPS spectra of Li (1s) for the cathode manganese dioxide (\(\gamma\)-\(\text{Mn}_2\)).

**I.R. Spectral Studies:** The IR Spectra of \(\gamma\)-\(\text{Mn}_2\), before and after discharge are shown in Fig. 7.

![Image](attachment:image3)

**Fig. 7.** FTIR spectra of the \(\gamma\)-\(\text{Mn}_2\) cathode before and after the first discharge cycle in \(\text{Zn}([\text{Mn}_2]\text{LiOH})\) aqueous battery. Peak labels A - main octahedral vibration and B, C - C-O in \(\text{Li}_2\text{CO}_3\).
The material before discharged had only one peak [11] at 670 cm\(^{-1}\). The discharged material showed strong broad bands at 1470 - 1520 cm\(^{-1}\) and a sharp peak at 875 cm\(^{-1}\). These could be assigned to lithium carbonate (Li\(_2\)CO\(_3\)) [12]. As noted above Li\(_2\)CO\(_3\) is the contaminant, which is formed by reaction of the LiOH electrolyte with atmospheric CO\(_2\). The spectra also has two strong absorption peaks “A” and “B” at 607 and 875 cm\(^{-1}\) respectively and a strong band “C” at 1470-1520 cm\(^{-1}\). The peaks below 800 cm\(^{-1}\) (Fig. 8) are assigned to fundamental vibrations of MnO\(_6\) octahedra [11].

![Graphs](image)

**Fig. 8.** FTIR spectra of γ-MnO\(_2\) cathode (a) before discharge (b) after discharge, and (c) chemically substituted LiMnO\(_2\).

The important thing to note here is that on discharge the material had an additional peak at 550 cm\(^{-1}\). This new peak is assigned to the Li intercalated MnO\(_2\) in which the Mn is in the Mn (III) oxidation state. This assignment is confirmed by preparing a sample of lithium intercalated MnO\(_2\) by the method described by K. Ishibashi [13] and recording its IR spectra under identical conditions. This is shown in Fig. 8 (c). Clearly the two spectra 8 (b) and 8 (c) are similar. Both show two peaks (A and A\(_1\) in figs. 8 (b) and 8 (c)) in the region 500 - 650 cm\(^{-1}\). This confirms that the product of discharge of γ-MnO\(_2\) is indeed lithium intercalated MnO\(_2\).

**Conclusion**

The characterization of the products formed when MnO\(_2\) is discharged in a Zn / MnO\(_2\) / LiOH cell, indicates that the cell discharge mechanism involves Li\(^+\) intercalation into γ-MnO\(_2\) host. The voltaic efficiency of the first discharge-charge cycle of the cell is 83%. However, the cathode material utilization is related to the number of charge / discharge cycles of the cell. It decreases with increasing cycle number. Typically the utilization drops to 39% at the 10\(^{th}\) cycle and then to 16% at cycle number 40. Thus, the reversibility and stability of γ-MnO\(_2\) in the aqueous LiOH cell is low.

**Acknowledgement**

One of the authors (M. Manickam) is grateful to Murdoch University for research fellowship and the conference travel award. The technical support of Ken Seymour, Stewart Kelly, and Doug Clarke, all of Murdoch University is also acknowledged.

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Electrochemical behavior of $\gamma$-MnO$_2$ in aqueous Lithium Hydroxide Electrolyte

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Introduction

The $\gamma$MnO$_2$ electrolytic manganese dioxide (EMD) has been investigated by several researchers as a cathode material for non-aqueous electrolyte lithium batteries. Even though, its use in aqueous Zn-MnO$_2$ batteries is well known in the literature, its use in lithium batteries in conjunction with aqueous LiOH electrolyte has not been seriously considered. In one of our recent papers we have reported that when aqueous LiOH electrolyte is used MnO$_2$ undergoes chemical changes, which are quite different from those reported for the aqueous KOH electrolyte [1]. In this case, the MnO$_2$ forms an intercalation compound of the formula LiMnO$_2$, which is similar to the product formed in non-aqueous electrolyte lithium batteries.

We have investigated this reaction further by subjecting $\gamma$-MnO$_2$ to cyclic voltammetry and analyzing the various products formed by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The results of this study are reported in this paper.

Experimental

The cathode consisted of a disk (1.2 cm$^2$) of MnO$_2$ mixed with conductive Carbon (A-99, Ashbury USA). The disk was embedded into a Pt gauze through which the electrolyte was made. The counter electrode was a zinc foil, which was separated from the main electrolyte by means of a porous foil. A saturated calomel electrode (SCE) was used as the reference electrode. The electrolyte was a saturated solution of lithium hydroxide.

The working electrode was cycled between 0.3 to -6 V, with a time starting at 0.3 V going instantly in the cathodic direction. For some experiments, the potential was held at an appropriate value for a defined period of time. An M/s 4PAR Potentialostat / Galvanostat model 273A, operated by model 270 software (EG&G) was used to monitor the potential at 25 $\mu$V $s^{-1}$ in all experiments. The products formed during the reduction of $\gamma$-MnO$_2$ were characterized by a Siemens X-ray diffractometer using a Phillips Co-K$\alpha$ radiation X-ray photoelectron spectroscopy (Kratos Ultra Axis Spectrometer) using monochromatic Al K$\alpha$ (1486.6 eV) radiation was used to obtain the chemical binding energy of the samples.

Results and Discussion

Figure 1 shows the cyclic voltammogram of $\gamma$-MnO$_2$ under the conditions noted in the figure. As can be seen in Fig. 1, the cyclic voltammetric profile consists of one broad peak $C_1$ and its corresponding oxidation peak $A_1$. A small shoulder at 46 mV is also seen during the reverse scan. The cathodic peak $C_1$ and anodic peak $A_1$ move at potentials $-480$ and $-160$ mV respectively. Although the potential difference between $C_1$ and $A_1$ is large ($\Delta$ Ep = 320 mV), the reaction is reversible.

The ratio of the charge under the peaks $C_1$ and $A_1$ is 0.81 suggesting that the reaction is 81% reversible. Figure 2 shows the X-ray analysis of the products formed when the potential of the $\gamma$MnO$_2$ working electrode was held constant at $-480$ mV for 0 min (Fig. 2a) 30 min (Fig. 2b) and 60 min (Fig. 2c). Due to poor crystallinity of the cathode material the X-ray diffraction pattern in Fig. 2 (a) shows a few Bragg reflections. As can be seen in Fig. 2 (b), the cathodic reduction of this material gives rise to two distinct sharp diffraction peaks at a d-spacing of 5.28 and 3.38 Å. When the time for which the potential is held at $-480$ mV is doubled to 60 min the diffraction peak corresponding to 5.28 Å decreases, whereas the peak corresponding to 3.38 Å increases in intensity. The peak at 5.28 Å is assigned to lithium intercalated $\gamma$MnO$_2$ that at 3.38 Å to lithium intercalated $\gamma$-MnO$_2$. The lithium intercalated $\gamma$-MnO$_2$ phase seems to dominate when the potential is held at $-480$ mV over longer periods. The XPS data of the same material as above indicate that the material is covered with a layer of Li$_2$CO$_3$. This is not unexpected because the atmospheric CO$_2$ is not excluded from the experiment. When the overlayer Li$_2$CO$_3$ is removed by Ar-ion bombardment, the Li$_2$CO$_3$ peak disappears but that of lithium intercalated $\gamma$-MnO$_2$ remains. This is consistent with what we have postulated earlier that the overlayer of Li$_2$CO$_3$ blocks the diffusion of O$_2$ but allows Li$^+$ ions to diffuse to the MnO$_2$ phase thereby forming lithium intercalated MnO$_2$. This observation has significance for developing lithium batteries using aqueous electrolytes.

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14th Australian Conference on Nuclear and Complementary Techniques of Analysis & 8th Vacuum Society of Australia Congress

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Electrochemical delithiation of LiMnPO₄ in aqueous battery system

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Abstract

The electrochemical behavior of lithium manganese phosphate (LiMnPO₄) as a cathode material has been investigated in a saturated aqueous lithium hydroxide electrolyte. The crystal structure and surface characterization of the olivine type LiMnPO₄ and the products which are formed on its oxidation and subsequent reduction were studied. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Scanning electron microscopy (SEM) and Secondary ion mass spectrometry (SIMS) were used for these investigations. LiMnP0₄ is found to be reversibly delithiated on electro oxidation.

Keywords: Aqueous battery, Delithiation, Olivine, Phosphate, Lithium manganese phosphate.

Introduction

Among the known Li extraction/insertion (delithiation/lithiation) compounds, the layered oxides LiCoO₂, LiNiO₂ and the spinel LiMn₂O₄ are now commercially used as cathode materials in rechargeable lithium batteries [1-3]. However, these materials suffer from poor electrochemical stability in their highly oxidized state [4]. In the case of LiMn₂O₄, the reduction of manganese below Mn⁵⁺ leads to a Jahn-Teller distortion. The major problem hindering the development of LiMn₂O₄ as a cathode material is the loss of capacity with extensive cycling [5]. Phosphate-based electrode materials, especially the phospho-olivines LiMPO₄ (where M = Fe, Mn, Co and Ni) are now recognized as attractive alternatives to oxide materials [6-9]. The presence of PO₄³⁻ polyanion with a strong P-O covalent bond in the olivine type structure provides a stable system when the electrode is charged. Since the pioneering study on LiFePO₄ by Padhi et al [7], significant work has been reported on the substitution of Fe with Mn, Co and Ni and their suitability as cathode materials in lithium batteries. LiMnP0₄ is an attractive cathode material owing to its high potential for use in batteries. Its electrochemical behavior in non-aqueous solvents has been reported in the literature [10-12].

In one of our previous paper [13], we reported a systematic study of the electrochemistry of LiFePO₄ in aqueous lithium hydroxide electrolyte. The objective was to establish how this material behaved as a cathode material in aqueous media in comparison to that in non-aqueous electrolytes. In this paper, we explore the electrochemical behavior of LiMnPO₄ for use in aqueous batteries.

Experimental

The material LiMnPO₄ (10 wt% carbon included) was received from Tokyo Institute of Technology and its cathode properties are reported elsewhere [14]. Analytical grade Zn foil (99.9%) from BDH chemicals, reagent grade LiOH.H₂O from Sigma Chemicals Company was used as received.

The experimental procedures for the cyclic voltammetric studies were similar to those reported earlier [13]. A standard calomel electrode (SCE) was used as the reference electrode and values are reported as such.

An EG&G PAR Potentiostat/Galvanostat model 273A, operated by model 270 software (EG&G) was used to scan the potential at 25 μV/s in all experiments. For X-ray analysis a Siemens X-ray diffractometer using Philips Co-Kα radiation was used. Kratos Ultra Axis Spectrometer using monochromatic Al Kα (1486.6 eV) radiation was used to analyze the chemical binding energy of the samples. The XPS analysis was started when the pressure in the analysis chamber fell below 1 x 10⁻⁶ hPa. The surface analysis of the materials was conducted by using a scanning electron microscope (Philips Analytical XL series 20). Secondary Ion Mass Spectrometry (SIMS) spectra were collected on a Cameca ims 5f instrument at the Australian Nuclear Science and Technology Organization (ANSTO), Lucas Heights, Sydney. An O₂⁺ primary ion source (12.5 KV) was used to generate secondary ions. A primary beam of 50 nA rastered over an area of 250 x 250μm was used in all experiments. The SIMS positive ion signals corresponding to Li was recorded.

Results and Discussion

Figure 1 shows the XRD profile of LiMnPO₄. The data matched with single-phase orthorhombic (olivine structure) as reported in the literature [7-8]. Its redox behavior can be seen from the cyclic voltammogram in the potential region -0.65 to 0 V in Fig. 2. The scan was initiated at -630 mV going first in the anodic direction to +100 mV and then reversing it back to the starting potential. An oxidation peak A₁ occurs at 65 mV in the anodic going portion of the CV. A cathodic peak C₁ is observed during the reverse scan at -480 mV. Thus the material undergoes electro oxidation/reduction presumably involving change of the oxidation state of the Mn atom in LiMnPO₄. The large gap
between the oxidation and reduction potentials seems to suggest that the process is not totally reversible in aqueous solutions.

Fig. 1 X-ray diffraction spectrum of the starting material LiMnPO₄

Fig. 2 A typical cyclic voltammogram of LiMnPO₄

With the objective of identifying the products formed on electro oxidation and reverse reduction, the following experiment was done. The material was subjected to electro oxidation in a three cell configuration under galvanostatic conditions (0.25 mA/cm²). The products formed were examined by XRD, SEM, XPS and SIMS. The electro oxidized material was then subjected to reverse reduction galvanostatically at the same current density. The resulting material was also analysed by using the same techniques as noted above.

X-ray diffraction spectra of the starting material LiMnPO₄ before oxidation and that after its electro oxidation are shown in Fig. 3. As can be seen from the figure 3, the XRD spectrum of the oxidized material differs significantly from that of the starting material. New reflections at 2θ =

Fig. 3 X-ray diffraction spectra of LiMnPO₄ (a) before and (b) after electro oxidation.

Fig. 4 SEM micrographs of LiMnPO₄ (a) before and (b) after electro oxidation.

22.5°, 35.0° and 42.0° are seen. These peaks are assigned to
MnPO₄ in accordance with the values quoted in the ICDD card No: 70-0180. The XRD pattern of the product formed on electro oxidation of LiMnPO₄ is indicative of the lower crystallinity of the product which in this case is delithiated MnPO₄. This is also reflected in the Scanning electron micrograph (SEM) of this material as shown in Fig. 4. The product has very different morphology compared to the material before the oxidation (Fig. 4).

Fig. 5 X-ray diffraction spectra of LiMnPO₄ (a) before electro oxidation (b) after electro oxidation and (c) after reverse electro reduction.

Fig. 6 XPS spectra of Mn 3s and Li 1s of LiMnPO₄ (a) before electro oxidation (b) after electro oxidation and (c) after reverse electro reduction.

Further confirmation of delithiation/lithiation of Li⁺ during oxidation/reduction of LiMnPO₄ is obtained from the secondary ion mass spectrometry (SIMS) analysis. The figure 7 shows changes in the Li⁺ ion count as obtained by SIMS analysis of the products formed on oxidation of LiMnPO₄ and its reverse reduction. The data shows that during oxidation the Li⁺ count is decreased and then increases on reverse reduction. This supports the delithiation mechanism for oxidation/reduction of LiMnPO₄.

Based upon, the results discussed above it can be concluded that the electrochemical oxidation of LiMnPO₄ result provides further evidence to reversible delithiation of LiMnPO₄ on oxidation.
leads to the phase MnPO₄ and on subsequent reduction reverts back to LiMnPO₄.

Conclusion

The preliminary electrochemical investigation of LiMnPO₄ in aqueous LiOH shows that delithiated MnPO₄ is formed when LiMnPO₄ is electro oxidized. This process is reversible. This is confirmed by the analysis of the products formed on electro oxidation / reduction of LiMnPO₄ by using XRD, SEM, XPS and SIMS.

Acknowledgement

We gratefully acknowledge Prof. Atsuo Yamada of Tokyo Institute of Tech. for providing a LiMnPO₄ sample. One of us (M.M.) is grateful to Murdoch University for a research Scholarship. The financial support of Australian Nuclear Science and Engineering (ANSE) for carrying out a part of the work at Australian Nuclear Science and Technology organization (ANSTO) is also acknowledged.

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Proceedings of the 10th Asian Conference on
SOLID STATE IONICS
ADVANCED MATERIALS FOR EMERGING TECHNOLOGIES
Kandy, Sri Lanka 12 - 16 June 2006
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ELECTROCHEMICAL LITHIUM INSERTION INTO A MANGANESE DIOXIDE ELECTRODE IN AQUEOUS SOLUTIONS

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Intercalation of lithium into the vacant sites of a host compound can be achieved electrochemically using non-aqueous 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 using aqueous solutions, lithium hydroxide as the electrolyte. The X-ray photoelectron spectroscopy (XPS), Scanning electron microscopy (SEM) and Secondary ion mass spectrometry (SIMS) data on the discharged material indicate that lithium is intercalated into the host structure of EMD without the destruction of its core structure. A significant improvement in cell performance was obtained by adding small amounts (< 3 wt%) of titanium disulphide (TiS₂) to the cathode.

Introduction

Lithium-ion batteries now represent the state-of-the-art in small-size rechargeable batteries for consumer electronic devices. Commercial lithium-ion batteries rely on the application of one of the well-known lithium intercalation hosts i.e., LiCoO₂, LiNiO₂, LiMn₂O₄ or γ-MnO₂ [1-4]. Recently, novel materials based on transition metal polyanions have also been proposed, and phosphate compounds crystallizing as Nasicon structures appear to hold particular promise [5-6]. For instance, it has been suggested that lithium iron phosphate, LiFePO₄, may offer the optimal combination of low cost, favorable electrochemical activity, and low environmental impact [7]. Lithium has been intercalated into these materials using non-aqueous electrolytes. The use of aqueous methods is less common because of the reactivity of many lithium intercalation compounds with water. In one of our previous papers [8] we reported that lithium could be intercalated into γ-MnO₂ from LiOH solution in an aqueous cell. Giovannini et al. [9] described γ-MnO₂ as an intergrowth structure between ramsdellite and pyrolusite, which are both members of the nsutite group. The basic unit cells are [MnO₆]octahedra joined to form alternating single- and double chains. Ruetzchi et al. [10] have summarized the types of MnO₂ materials to be considered important for batteries, among these electrolytically produced manganese dioxide (EMD) is widely used commercially.

In traditional alkaline batteries using KOH as the electrolyte MnO₂ is not suitable for its reversibility, because during discharge the electrode reaction involves the insertion of protons into the ionic lattice of the manganous oxide according to the equation:

\[ \text{MnO}_2 + \text{H}^+ + e^- \rightarrow \text{MnOOH} \]  \hspace{1cm} \text{Eq. [1]}

Whereas, the use of aqueous LiOH as an electrolyte results in the incorporation of lithium ions into the MnO₂ structure during the discharge.

\[ \text{Li}^+ + e^- + \text{MnO}_2 \rightarrow \text{LiMnO}_2 \]  \hspace{1cm} \text{Eq. [2]}

The overall reaction of the alkaline Zn/MnO₂ battery using LiOH electrolyte is

\[ \text{Li}^+ + e^- + \text{MnO}_2 \rightarrow \text{LiMnO}_2 \]  \hspace{1cm} \text{Eq. [3]}

This reaction in Eq. 3 is similar to that for Li/MnO₂ non-aqueous batteries except that it exhibits slow reversibility. During cell discharge, Li⁺ ions are inserted into the γ-MnO₂ structure, causing the reduction of Mn³⁺ ions to Mn²⁺ ions. During oxidation, the γ-MnO₂ reverts to its original phase upon the extraction of Li⁺ ions from the structure. However the rate of reversibility is slow due to the formation of Mn₃O₆. The main objective of this paper is to report our findings on

1. Electrolytically produced manganese dioxide (EMD) and to compare with chemically prepared battery grade manganese dioxide (BGM) in aqueous solutions. The purpose is to determine whether the BGM behaved in a manner similar to EMD.
2. Improvement in cell performance by adding small amounts (< 3 wt%) of titanium disulphide (TiS₂) to the cathode.

Experimental

The γ-MnO₂ of EMD type and BGM used in this work were purchased from the Foote mineral company and Sigma Aldrich, respectively. The cell design and experimental details were similar to those reported earlier [8-11]. The cells were discharged/charged galvanostatically at 0.5 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 1.9 V, respectively. All electrochemical measurements were carried out at ambient atmosphere. The products formed during charge and discharge cycles were characterized by a Siemens X-ray diffractometer using Philips Co-Kα radiation. X-ray photoelectron spectroscopy (Kratos Ultra Axis Spectrometer) using monochromatic Al Kα (1486.6 eV) radiation was used to analyze the chemical binding energy of the samples. X-ray photoelectron spectroscopy (XPS) analysis was started when the pressure in the analysis chamber fell below 1 x 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). Secondary Ion Mass Spectrometry (SIMS) spectra were collected on a Cameca ims 5f instrument at the Australian Nuclear Science and Technology Organization (ANSTO), Lucas Heights, Sydney. An O₂⁻ primary ion source (12.5 KV) was used to generate secondary ions. A primary beam of 50 nA rastered over an area of 250 x 250μm was used in all experiments. The SIMS positive ion signals corresponding to ¹²Li was recorded.
Results and Discussion

Performance characteristics of Zn-\(\gamma\)-MnO\(_2\) of EMD type aqueous LiOH cell:
The performance characteristics of MnO\(_2\) in alkaline aqueous Zn-MnO\(_2\) cells containing potassium hydroxide (KOH) as the electrolyte have been reported extensively in the literature [12-14]. Kordesch [14] has reported that the discharge behavior of the cathode material, MnO\(_2\), in the alkaline KOH electrolyte occurs in a heterogeneous phase reaction, i.e. MnO\(_2\) being converted to Mn\(_2\)O\(_3\). Hence, the MnO\(_2\) lattice expands and, at a certain point of discharge, the mechanism changes to an irreversible portion of the MnO\(_2\) reduction process. We have investigated the use of LiOH in place of KOH in alkaline Zn - MnO\(_2\) cells. Zn/ MnO\(_2\)/ LiOH (aq.) cells were discharged at constant current density (0.5 mA/cm\(^2\)) to 1 V cut-off. For comparison, cells containing KOH in place of LiOH were also discharged under identical conditions. Each of the electrolytes contained 1 M ZnSO\(_4\) in addition to the saturated solutions of LiOH or KOH. The results for the first discharge cycle for both the cells are shown in Fig. 1. The cell containing LiOH discharged at a higher voltage and had a higher material utilization compared to the cell with KOH electrolyte. The cathode utilization for the LiOH cell was found to be 56% (162 mAh/g) as compared to 41% (120 mAh/g), for the KOH cell.

![First discharge curve of Zn-MnO\(_2\) (EMD type) cells using saturated aqueous of (a) KOH and (b) LiOH containing 1 mol. L\(^{-1}\) of ZnSO\(_4\) under identical conditions.](image)

The reversibility of the cell Zn-MnO\(_2\) using sat. LiOH as the electrolyte was investigated and their results are shown in fig. 2. The cell could be reversibly discharged and charged. The cathode material utilization was calculated from the initial weight of the active MnO\(_2\) in the cathode and the voltaic efficiency from the observed average charge/discharge voltages. The material utilization of 56% (162 mAh/g) for discharge and 54% (156 mAh/g) for charge and the voltaic efficiency of 83% were obtained. Figure 3 shows the variation of open-circuit voltage versus number of cycles. For the first cycle the open-circuit voltage was 1.8 V and then for the 10th cycle the OCV falls to 1.785 V and for subsequent cycles it decreases to 1.713 V.

![Cycling behavior of the Zn-MnO\(_2\) (EMD type) battery over subsequent cycles.](image)

![Variation of the open-circuit voltage vs. cycle number for the Zn - MnO\(_2\) (EMD type) battery.](image)

![Scanning electron micrographs of the MnO\(_2\) (EMD type) cathode material.](image)

The investigation on the surface morphology that occurs on the cathode material during the process of discharge and recharge has substantially confirmed the presence of a new material as seen in fig. 4. The morphology of as-prepared MnO\(_2\) fig. 4 a, revealed that the particle size of the order of 20-25 \(\mu\)m. The material formed after the discharge had a very different morphology (fig. 4 b). The particle size was of the order 40-50 \(\mu\)m. It appears that during discharge the
original γ-MnO₂ particles agglomerate into larger particles perhaps containing lithium ions intercalated into the material. The micrograph (fig. 4 c) for recharged sample 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 battery capacity after few cycles, as shown in the cycling behavior, fig. 2. In order to confirm the existence of lithium ions in the solid matrix of the discharged cathode material it was subjected to XPS and SIMS studies. As reported earlier [8], before the XPS and SIMS analysis, the surface of the cathode material was ion bombarded to remove the thick layer of materials (like LiOH, Li₂CO₃ and H₂O) on the surface of the discharged products. LiOH is present because the material is discharged in LiOH, which remains adsorbed at the surface. The lithium carbonate is the result of LiOH reacting with atmospheric carbon dioxide. After ion bombardment, the spectrum shown in Fig. 5 was recorded. The peak at 54.7 eV could be assigned to intercalated lithium [15] into the MnO₂ host structure. To investigate the lithium distribution in the bulk sample MnO₂ the depth profile was carried out. Figure 6 represents the depth profile results for a discharged cathode. It can be seen that while going from surface to bulk, Mn species decreased while Li species slightly increasing in lithium counts. This result agrees with the XPS studies that lithium is present in the structure.

Fig. 5 XPS spectra of Li (1s) for the cathode MnO₂ (EMD type). Time in figure indicates the etching duration.

Fig. 6 SIMS depth profile of discharged MnO₂ (EMD type)

Performance characteristics of Zn- BGM- aqueous LiOH cell: Figure 7 shows the difference in the discharge characteristics of the cells containing EMD and the BGM as cathode materials. The open circuit voltage of BGM is higher and the discharge voltage profile is flatter than that for the EMD material under identical conditions. The rate of voltage drop during discharge is almost identical. The delivered discharge capacity for these two materials is almost identical at a 1 V cut-off voltage (ca. 165 mAh/g). In contrast to EMD the BGM shows a sharp drop in voltage, whereas the EMD does not show such drop up to that point. This is probably related to the difference in the composition of the two MnO₂ materials with respect to ramsdellite and pyrolusite, water content and surface area. The BGM exhibit quite different rechargeability when subjected to continuous discharge/charge cycles. As seen in Fig. 8, a 35% drop in the active material utilization occurred at cycle number 2 for this cell. For EMD, the same drop occurred at the 20th cycle (Fig. 2). Thus the EMD is more stable to discharge/charge cycling.

![Fig. 7 Comparison of the two different MnO₂ on their first discharge voltage profiles](image1)

![Fig. 8 Voltage vs. discharge capacity of Zn(MnO₂-BGM|LiOH cells on the second cycle](image2)

Additive of TiS₂ in the EMD cathode: Following the incorporation of the Bi³⁺ additive, several other additives have been explored [12, 16]. A potential candidate in this regard has been been Ti³⁺ ion [16]. This is usually done by anodic deposition of EMD from an acidic solution of manganese sulphate containing some Ti³⁺ ions. In this work, small amounts of TiS₂ as additives have been employed by physical mixing into EMD and investigated their electrochemical behavior. The SEM micrograph (fig. 9) with the additive of 5 wt% shows a change in morphology i.e. rounded particles around 10μm in diameter. Figure 10 shows the cell performance of the MnO₂ cell by adding various amounts of TiS₂. A significant improvement in discharge capacity was obtained by adding amounts (< 3 wt %) of titanium disulphide (TiS₂) to the cathode. This could be explained in terms of the doping ions known to stabilize the MnO₂ structure towards dimensional changes that occur during the discharge process. However, increasing the doping content from 3 to 5 wt % causes a decrease in the cell capacity. Although not fully understood, increasing the doping content could modify the “open structure” configuration of MnO₂ for intercalation. This probably could be related to the change in surface morphology as reflecting via the SEM micrograph in Fig. 9.
Conclusions
The characterization of the products formed when MnO₂ is discharged in a Zn|MnO₂|LiOH cell, indicates that the cell discharge mechanism involves Li⁺ intercalation into the host structure. As compared to battery grade material (BGM), electrolytic manganese dioxide (EMD) is found to be more stable to discharge/charge cycling. The incorporation of small amounts of TiS₂ additives into MnO₂ is found to improve the discharge capacity. However, increasing the doping content from 3 to 5 wt% causes a decrease in the cell capacity.

Acknowledgements
The author M. Manickam is grateful to Murdoch University for a research scholarship. The financial support of Australian Nuclear Science and Engineering (ANSE) for carrying out a part of the work at Australian Nuclear Science and Technology (ANSTO) is also acknowledged. The author would like to thank Peter Fallon of Murdoch University for his technical support.

References
Appendix (C)

Papers presented in conferences but not published
Postgraduate Research Conference
2003

2nd October, Ascot Inn, Perth, Western Australia
X-ray Photoelectron Spectroscopy Studies of Lithium Insertion into Manganese Dioxide Cathode Material in Aqueous Lithium Hydroxide Electrolyte Batteries

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Electrochemical intercalation of lithium into the host framework structure of a manganese dioxide cathode material (γ-MnO₂ of EMD type) in a battery, which uses aqueous LiOH electrolyte has been investigated. X-ray photoelectron spectroscopy (XPS), a powerful tool for surface studies, has been used to analyze the cathode material obtained after it has been fully discharged in the battery. The material was found to be covered with a film of water (O 1s) which acted as a double layer and hence prevented detection of other elements by the XPS analysis. The material was thus bombarded with Ar⁺ ions for 60, 120, 240 and 480 min to remove the water overlayer. After the ion bombardment, the intensity of the oxygen (O 1s) peak corresponding to the water content overlayer decreased. This enabled detection of the presence of Manganese (Mn 3s) and Li (1s) and Li₂CO₃ in the resulting material.

The results showed that lithium is indeed intercalated electrochemically into the host framework structure of γ-MnO₂ when aqueous LiOH is the electrolyte. Thus in aqueous LiOH, the EMD undergoes a discharge reaction which is quite different from the one commonly reported for batteries which use aqueous KOH electrolyte.
Abstract Book
THE 12TH ROYAL AUSTRALIAN CHEMICAL INSTITUTE (RACI) CONVENTION
Sydney Convention and Exhibition Centre,
Darling Harbour, Australia
Sunday 3 July to Thursday 7 July 2005
T078 PO EI  ELECTROCHEMICAL BEHAVIOR OF LIFEP04 IN AQUEOUS LITHIUM HYDROXIDE ELECTROLYTE

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Phosphate-based olivine materials such as LiFePO4 have been extensively investigated for their use as cathode materials in non-aqueous electrolyte lithium batteries. We have carried out a study of the electrochemistry of LiFePO4 in aqueous lithium hydroxide (LiOH) electrolyte with the objective of establishing whether this material could also be used as a cathode material in aqueous electrolyte batteries. Another objective was to determine how this material compared with MnO2 and TiO2 for the same application. LiFePO4 when scanned anodically showed an oxidation peak at -42 mV vs. saturated calomel electrode (SCE). The x-ray diffraction pattern of the product of this oxidation indicated the formation of a mixture of Fe (III) compounds. The products formed during the subsequent reverse cathodic scan consisted of Fe(OH)3 and Fe3PO4 phases. Thus the oxidation/reduction of LiFePO4 did not involve reversible lithium ion intercalation mechanism. In this regard, LiFePO4 behaved very different from MnO2 and TiO2 for which we previously reported to undergo reversible lithium intercalation during reduction/oxidation in aqueous LiOH electrolyte. The paper describes the results and discusses implications of the findings.

T079 PO EI  SURFACE CHARACTERISATION OF HEAT-TREATED ELECTROLYTIC MANGANESE DIOXIDE

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In this work an acid-base titration technique was used to determine the amphoteric properties of a variety of electrolytic manganese dioxide (EMD) materials. This technique along with other testing, including electrochemical analysis, x-ray diffraction and BET, were used to determine the effect that the bulk structure has on the surface properties of the EMD. This work includes studies on the following series: i) Heat treatment of an industrial EMD up to 500°C; ii) A range of MnO2 and iii) A series of EMD's produced under varying synthesis conditions. The study found that the surface consisted of independent acidic and basic hydroxyl sites which can be characterised by their equilibrium constants and site concentrations. It was discovered that the acidic sites could be in fact characterised by a distribution of equilibrium constants dependant on pH, while the basic sites could be represented by a single equilibrium constant. Ks values ranged from 0.1 to and 6.3 x 10^5 while Km was found to be 1.81 x 10^7. It was observed that both Ks and Km values rose with increased heat-treatment, these trends were rationalised by the structural changes occurring within the material shown by the analysis of physical testing. The electrochemical analysis showed a decrease in performance with increased temperature of heat treatment. From comparing this finding with the titration results it was concluded that the proton insertion occurred only through basic surface sites of the EMD.
Extended Abstracts of
The 25th Electronics Division Meeting

Tokyo Institute of Technology, Tokyo, Japan
October 27-28, 2005

第25回エレクトロセラミックス研究討論会

講演予稿集
（付録：電子材料部会ニュースレター NO.10）

開催日：2005年10月27日（木）～28日（金）
会場：東京工業大学大岡山キャンパス西9号館（東京都目黒区）
主催：(社)日本セラミックス協会・電子材料部会
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電子情報通信学会、日本化学会、日本材料学会
日本材料科学会、粉体粉末冶金協会

Published by the
Ceramic Society of Japan

社団法人 日本セラミックス協会
Electrochemical behavior of LiFePO$_4$ in aqueous lithium hydroxide electrolyte

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Abstract
The electrochemistry of olivine iron phosphate (FePO$_4$) as a battery cathode material in aqueous lithium hydroxide (LiOH) has been investigated. The material forms intercalated LiFePO$_4$ reversibly on electrodereduction/oxidation. The formation of Fe$_2$O$_3$ phase in addition to the regeneration of FePO$_4$ during reverse oxidation of LiFePO$_4$ also occurs. In this regard, the mechanism of FePO$_4$ discharge/charge in aqueous LiOH differs from that in non-aqueous solvents.

Introduction
Recently, phosphate-based olivine materials have generated considerable interest as a new class of cathode materials for lithium-ion rechargeable batteries which use non-aqueous electrolytes. In particular, iron based phosphate which has a high voltage and is eco friendly has been investigated for use in electric vehicles [1]. However, very little is known about the electrochemical behavior of this material in aqueous media. In this paper, we report the results of our study on the electrochemical behavior of olivine FePO$_4$ in saturated LiOH electrolyte.

Experimental
The experimental procedures were similar to those reported earlier [2].

Results and Discussion
Figure 1 shows the discharge profile of FePO$_4$. The shape of the discharge curve is characterized with an initial voltage of 1.4 V which gradually decreases to 1.0 V followed by a sharp drop. The realizable capacity of the material is approximately 70 mAh/g.

The X-ray diffraction spectra of the FePO$_4$ before and after discharge are shown in Fig. 2. The data for the undischarged FePO$_4$ suggests that the material was amorphous. The spectra of the same material after discharge (fig. 2b) suggests that a crystalline phase is formed. This phase is identified to be LiFePO$_4$ which is consistent with what is reported to be formed in non-aqueous media. This indicates that the electro reduction of FePO$_4$ involves lithium intercalation forming LiFePO$_4$. The XRD spectrum of the material formed on re-oxidation indicate that the starting material FePO$_4$ is regenerated suggesting that the intercalation process is reversible. However, a presence of an additional phase corresponding to Fe$_2$O$_3$ is also detected in this spectrum. In this respect, the mechanism of electro reduction/oxidation is different from that in non-aqueous media.

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