Electrochemical Behavior of Solid Lithium Manganate (LiMn$_2$O$_4$) in Aqueous Neutral Electrolyte Solutions

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Received January 10, 2003. In Final Form: July 17, 2003.

Lithium manganate (LiMn$_2$O$_4$) was synthesized by a very simple low-temperature solution combustion technique. The product was characterized for its phase formation and composition by X-ray diffraction and inductively coupled plasma spectroscopy. The electrochemical behavior of this material in aqueous neutral electrolyte solutions was investigated in an effort to find a means of making it a usable electrode material for rechargeable battery systems in aqueous electrolytes. Cyclic voltammetric and chronopotentiometric studies of solid LiMn$_2$O$_4$ immobilized on a paraffin-impregnated graphite electrode were carried out in various aqueous neutral electrolyte solutions. LiMn$_2$O$_4$ was shown to undergo reversible insertion of K$^+$, Li$^+$, and NH$_4^+$ ions from neutral electrolyte solutions. Energy-dispersive X-ray (EDX) detection of electrochemically treated LiMn$_2$O$_4$ proved the presence of the intercalated K$^+$ ion. The intercalation of the K$^+$ ion was partial, as is shown by the weight percent analysis of EDX detection results.

Introduction

The electrochemistry of LiMn$_2$O$_4$ in nonaqueous electrolytes has been extensively studied as a cathode material for rechargeable lithium batteries and, more specifically, for the rocking-chair type with carbon as the negative electrode. Lithium insertion characteristics of LiMn$_2$O$_4$ in nonaqueous electrolytes have been the subject of detailed investigations as a result of their importance in deciding the stability and reversibility in cycling.\textsuperscript{1,2} Lithium can be inserted into or extracted from spinels by electrochemical or chemical redox reactions. The extraction of lithium from LiMn$_2$O$_4$ results in Li$_x$Mn$_2$O$_4\textsuperscript{3,4}$ This insertion induces the Jahn-Teller distortion of Mn$^{3+}$ ions, favoring the phase transition from a cubic to a tetragonal structure. On the basis of NMR studies of lithium ion insertion into Li$_x$Mn$_2$O$_4$, Kanzaki et al. hypothesized that the Li exists in the atomic state but not in the ionic state. They also interpreted a Kanzaki et al. hypothesized that the Li exists in the atomic + state but not in the ionic state. They also interpreted a

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\textsuperscript{2} Thackeray, M.; de Picciotto, L.; de Kock, A.; Johnson, P.; Nicholas, V.; Dendorff, K. J. Power Sources 1987, 21, 1.


In the present work, LiMn_2O_4 was synthesized by a low-temperature solution combustion technique and its composition was analyzed by X-ray diffraction (XRD) and inductively coupled plasma spectroscopy (ICP). To understand the intercalation electrochemistry of LiMn_2O_4, low-temperature solution combustion technique and its decomposition was analyzed by X-ray diffraction (XRD) and to screen the material for its feasibility as an active battery electrode. To prove the metal cation intercalation, energy-dispersive X-ray (EDX) analysis of electrochemically treated samples of LiMn_2O_4 was carried out.

**Experimental Section**

**Preparation of LiMn_2O_4 by the Low-Temperature Solution Combustion Technique.** In this method, attention should be given to calculating the stoichiometric composition of oxidizing and reducing species to obtain phase-pure final products and also to avoid the evolution of undesired gases such as NO_2 during the combustion process. The stoichiometric compositions of the redox mixtures for the combustion reaction are calculated using the oxidizing (O) and reducing (R) valencies of the individual components, which serve as the numerical coefficients for the stoichiometric balance, so that the equivalent ratio, R_n, is unity (i.e., O/R = 1) and the energy released by combustion is a maximum. On the basis of the concept used in propanolic chemistry, the elements H, C, and M (Li, Mn) are considered reducing species with valencies +1, +4, +1 (Li), and +2 (Mn), respectively. The oxygen is considered an oxidizing species with a valency of 0, and the valency of nitrogen is considered 0. Accordingly, the oxidizing valencies of the LiNO_3 and Mn(NO_3)_2 compounds become −5 and −10, respectively, and the reducing valency of urea (NH_2CO−NH_2) is +6. To get the value of R_n = 1, the moles of urea to be taken is calculated as

\[
\text{oxidizing valencies of LiNO}_3 + 2\text{Mn(NO}_3)_2/\text{reducing valency of urea}
\]

That is, (5 + 20)/6 = 4.166. The stoichiometric equation for the synthesis of LiMn_2O_4 can be written as

\[
\text{LiNO}_3 + 2\text{Mn(NO}_3)_2 + 4.2\text{NH}_3\text{CO}−\text{NH}_2 \rightarrow \text{LiMn}_2\text{O}_4 + 13.4\text{N}_2 + 4.2\text{CO}_2 + 8.4\text{H}_2 + 3.4\text{O}_2
\]

In a typical experiment, Mn(NO_3)_2·4H_2O (3.837 g), LiNO_3 (2.298 g), and urea (8.4 g) were dissolved in 50 mL of distilled water in a 500-mL glass beaker. The beaker was placed in a resistance-heated muffle furnace maintained at 500 °C. After a few minutes, the solution boiled and underwent rapid dehydration followed by decomposition with an intense flame to yield a fine black powder of LiMn_2O_4 (5.8 g). All the chemicals used were of analytical grade, and the solutions were prepared with double-distilled water.

**Equipment and Measurements.** For electrochemical measurements, the following instrumentation was used: an Autolab (Eco-Chemie, Utrecht, The Netherlands), an electrode stand VA 663 (Metrohm, Herisau, Switzerland), and a personal computer. The reference electrode (Metrohm, Switzerland) was an Ag/AgCl electrode with 3 M KCl (E = 0.208 V vs standard hydrogen electrode). Platinum wire was used as counter electrode. The solid LiMn_2O_4 powder was mechanically immobilized on the surface of the paraffin-impregnated graphite electrode (PGE) and used as the working electrode. All the measurements were performed in solutions which were thoroughly deaerated with high-purity nitrogen for at least 10 min. The voltammograms were recorded at 22 ± 1 °C. XRD measurements were performed with a HZG 4 (Seifert-SPM, Germany), and the scanning electron microscope (Leo 440, Germany) equipped with an E Colon 4 detector (EDAX, U.S.A.) was used for the chemical analysis of the electrochemically treated samples of LiMn_2O_4.

**Results and Discussion**

**XRD Studies.** The XRD pattern of the LiMn_2O_4 sample prepared by the solution combustion technique is comparable with the standard Joint Committee on Powder Diffraction Standards data and shows the formation of a single-phase compound (Figure 1). It is reported in the literature that LiMn_2O_4 belongs to the spinel system with cubic symmetry (Fd3m). The chemical composition obtained by ICP analysis was Li_{0.90}Mn_{2.04}O_4. The deviation from the stoichiometry is due to the generation of a high temperature during the combustion, where volatilization of lithium loss can be expected. Our attempt to prepare stoichiometric LiMn_2O_4 by varying the lithium as well as urea concentrations by this method was not successful. The effect of the temperature on the synthesis of various Li_{1−x}Mn_{x}− based oxide materials was reported by Lee et al. in the literature.

**Electrochemical Studies.** Before entering into the discussion part of explaining the origin of the two redox couples that appeared for LiMn_2O_4 in neutral electrolyte solutions, the stability of this compound in this pH and potential range has to be established. This exercise was necessary because the aqueous electrochemistry of this...
compound was almost negligible, and the possibility of LiMn$_2$O$_4$ undergoing dissolution to produce the redox peaks in cyclic voltammograms cannot be excluded. From the potential–pH diagram of the LiMn$_2$O$_4$ system, the hypothetical standard electrode potential of Li$^+$/LiMn$_2$O$_4$ is 0.73 V versus the normal hydrogen electrode. However, the experimental work done in the nonaqueous system does not validate this value. It was reported to be +4.2 V versus the Li$^+$/Li (metal) reference system, which was higher than the theoretical value of 3.73 V. This lack of coincidence is understandable because the preparation procedure concurrently affects the structure, morphology, and composition of the compound. The same fact influences the electrochemistry of LiMn$_2$O$_4$ in an aqueous medium. In an earlier work, MnO$_2$ was subjected to cathodic behavior of the thin-film LiMn$_2$O$_4$ electrode in aqueous $\text{MnO}_2$ particles. Recently, electrochemical behavior of the thin-film LiMn$_2$O$_4$ electrode in aqueous media has been investigated, and the results indicate that the electrode was highly stable in aqueous media. On the basis of the above evidences and inferences, we conclude that LiMn$_2$O$_4$ was stable within the potential limits and pH range of our experiment.

A few micrograms of solid LiMn$_2$O$_4$ powder synthesized by the solution combustion method was mechanically immobilized on the surface of the PIGE. This technique is highly useful in determining the electrochemical characteristics of any new solid material because it need not be subjected to mechanical, physical, and chemical pretreatments. Cyclic voltammetric experiments in various concentrations of LiCl, KCl, and NH$_4$Cl electrolyte solutions and between the potential limits of $-1$ to $+1.5$ V versus Ag/AgCl were recorded. The scan rate employed was 0.05 V s$^{-1}$. Figure 2 shows the typical cyclic voltammograms obtained for the LiMn$_2$O$_4$ in 0.1 M KCl, LiCl, and NH$_4$Cl solutions. The cyclic voltammograms show two sets of redox peaks in all the electrolyte solutions. The formal potentials evaluated from the redox couples I–IV and II–III are presented in Table 1. The Li$^+$ ion, being the most electronegative cation, gets intercalated at more negative potentials compared to the K$^+$ and NH$_4^+$ ions. Hence, the increasing order of preference for cation intercalation in the LiMn$_2$O$_4$ lattice during electrochemical cycling was Li$^+ >$ K$^+ >$ NH$_4^+$. The observed difference in the formal potentials is due to different degrees of hydration of these cations. With an increase in concentration of the electrolyte solutions, the formal potentials for the redox couple I–IV increases in all three cases. However, for the K$^+$ and NH$_4^+$ ions against the Li$^+$ ion, the formal potentials of the second redox couple decreases with an increase in the concentration of the respective electrolyte solution. This could be due to the competitive proton insertion/extraction process that takes place with more ease in the presence of the K$^+$ and NH$_4^+$ ions. The shift of the electrode potentials toward the positive direction indeed indicates an increase in the free energy for the redox reaction.

We believe that the redox peaks I and IV in the cyclic voltammograms in Figure 2 were due to the intercalation and deintercalation of the respective cations. Considering a typical example of the intercalation of the potassium ion, the equation for the redox reaction represented by peaks I and IV may be written as

$$
\text{xK}^+ + \text{LiMn}_2\text{O}_4 + \text{xe}^- \rightarrow \text{Li}_{1-x}\text{K}_x\text{Mn}_2\text{O}_4
$$

In accordance with the Nernst law, this reaction should follow the dependence of the formal potential on the activity of the potassium cation:

$$
E_f = E^0 + 0.059 \log a_K.
$$

That is, the formal potential $E_f = (E_a + E_c)/2$ ($E_a$, anodic peak potential; $E_c$, cathodic peak potential) of the redox reaction should be directly proportional to the concentration of $\text{K}^+$ ions in the KCl electrolyte solutions. This is found to be the case in all three electrolytes. Figure 3 shows the derived plots of $E_f$ versus log [M$^+$] $\{[\text{M} = \text{K}, \text{Li}, \text{NH}_4]\}$, where the straight line graph has a positive slope. The formal potentials taken to derive this plot were from the redox couple I–IV. So, in solid LiMn$_2$O$_4$, reversible intercalation of Li$^+$, K$^+$, and NH$_4^+$ ions takes place from neutral electrolyte solutions.

In nonaqueous electrolytes, LiMn$_2$O$_4$ was proved to undergo lithium insertion and reinsertion via two processes that were independent of each other. In the present study dealing with the electrochemical behavior of LiMn$_2$O$_4$ in aqueous neutral electrolytes, cation intercalation takes place in two steps, as was realized by the two sets of redox couples shown in Figure 2. To understand

### Table 1. Formal Potentials of the Mn$^{3+/4+}$ System of Solid LiMn$_2$O$_4$ at Various Concentrations of KCl, LiCl, and NH$_4$Cl Electrolyte Solutions

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$E_f$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>1012</td>
</tr>
<tr>
<td>LiCl</td>
<td>800</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>153</td>
</tr>
</tbody>
</table>

The formal potentials are derived from the redox couples I–IV and II–III in all three cases. The shift of the electrode potentials toward the positive direction indeed indicates an increase in the free energy for the redox reaction.
the electrochemistry of this system, it was necessary to verify whether the redox processes taking place were interdependent or independent of each other. If the redox processes, whatever they may be, occur independently, then the scanning of LiMn$_2$O$_4$ in their respective potential regions should produce redox peaks irrespective of one another. In the case of cation intercalation being a continuous process, the previously mentioned exercise would yield an electrochemical spectrum different from that in Figure 2. The results obtained out of this exercise were interesting and contrary to that in nonaqueous electrolytes. Cyclic voltammograms obtained in the two redox couple regions between the potential limits of $-1.0$ to $+0.5$ V and $+0.5$ to $+1.3$ V are shown in parts A and B of Figure 4, respectively. In Figure 4A, there was a single oxidation peak in the forward scan but no reduction peak in the reverse scan. In Figure 4B, there were no peaks either in the forward or in the backward scans. This result led us to the conclusion that peak II in the oxidation scan was formed as a result of subsequent oxidation of the resultant product at peak I. The oxidized product at peak II gets reduced at peak III, which again subsequently undergoes further reduction at peak IV. This continuity in the redox process gets perturbed when there is a discontinuity in the potential cycling, as is shown in Figure 4A,B.

In addition to the cyclic voltammetric experiments, LiMn$_2$O$_4$ was subjected to chronopotentiometric experiments in a 0.1 M KCl solution. This was done in view of providing supportive evidence to the two-step intercalation process observed in this work. Because the electrochemistry of LiMn$_2$O$_4$ in the aqueous medium was not well-studied, it becomes essential to confirm and augment the electrochemical results obtained through cyclic voltammetric experiments by some other electrochemical techniques. In chronopotentiometry, the variation of the potential of LiMn$_2$O$_4$ with time upon the application of a constant current was studied. A basic assumption is made that all the applied current initiates the reaction between LiMn$_2$O$_4$ and alkali metal cations in the solution, and the mass transfer is controlled by the diffusion of these cations. Although the change in the bulk concentration is negligible during the transient, the concentrations of both the reactant and the product at the electrode surface vary markedly, and the ratio

$$C_{\text{ox}}(x = 0)/C_{\text{red}}(x = 0)$$

determines the observed potential. Eventually, the concentration of [ox] at the electrode surface has been reduced to 0, and diffusion is insufficient to supply enough reactant to satisfy the imposed current. At this point (the transition time), a large part of the current again charges the double layer and the potential shifts rapidly to a value at which some other electrode reaction occurs. During the passage of constant current, plateaus parallel to the $x$ axis appear at the corresponding potential of the redox reaction of interest as steps that could be related to peaks in a cyclic voltammogram. Upon current reversal, the redox reaction proceeds in the opposite direction and the nature of the reversibility of a system can be determined. For battery electrodes such as Fe/Ni-Fe alkaline cells, this transient technique was extensively employed to understand the discharge behavior of iron in the presence of additives and to calculate the percentage utilization of active material. Recently, for solid-state cells employing
which the reaction occurs. So, it becomes all the more
difficult to ascertain a particular reason to explain the
abnormal behavior of cation intercalations. The formal
potentials of the redox peaks of I and III in the cases of
K\(^+\) and NH\(_4\)\(^+\) ions decrease with an increase of the
concentration of the electrolyte solutions, as is evidenced
from Table 1. This could be as per the Nernst law as a
result of proton intercalation taking place in these peak
regions, as was established in the cases of LiNiO\(_2\),
LiCoO\(_2\),\(^{11,12}\) and LiMn\(_2\)O\(_4\).\(^{10}\) Then the redox reactions
responsible for the redox couples I–V and II–III may be
represented by eqs 1 and 2 as

\[
xK^+ + LiMn_2O_4 + xe^- \rightarrow Li_{1-x}K_xMn_2O_4 \quad (1)
\]

\[
xH^+ + LiMn_2O_4 + xe^- \rightarrow Li_{1-x}H_xMn_2O_4 \quad (2)
\]

In accordance with the literature and experimental
evidence, we put forward the previous scheme of redox
equations for the two-step intercalation of the cations,
each step corresponding to its occupation in two different
sites of crystal structure. Having established this fact,
the next step was to solve the puzzle of why the redox
couples were interdependent of one another, as was
evidenced in Figure 4. At the LiMn\(_2\)O\(_4\)/solution interface,
when the oxidation step involving the formation of peak
I occurs as a result of anodic polarization, K\(^+\) ions,
electrons, and water molecules coexist until further
polarization proceeds. Upon the continuation of anodic
polarization, potassium ions may get adsorbed at some
site (S) of the lithium manganese electrode surface and
react with water molecules to produce protons and
hydroxyl ions as represented by the following equations:

\[
K^+ + e^- \rightarrow KS
\]

\[
KS + H_2O \rightarrow K^+ + S + H^+ + OH^- 
\]

The resultant protons formed out of this reaction undergo
the intercalation process to form peak II as

\[
H^+ + LiMn_2O_4 + e^- \rightarrow LiHMn_2O_4 
\]

This phenomenon explains why the redox couples I–IV
and II–III were interdependent on one another and why
we did not observe any peaks in Figure 4B when the
experiment was carried out in that particular potential
range. Because of the above changes taking place at the
interface, the pH at the interface varies substantially from
that of the bulk pH, which provides a favorable condition
for the intercalation of protons in lithium manganate.

Though this kind of mechanism appears to be new in
intercalation electrochemistry, it is a well-known phe-
nomenon in passivation and corrosion aspects of elec-
trochemistry. To cite a few examples, it was observed that
on solid iron, the rate of hydrogen evolution decreases
with an increase of the

consumption of the Annual Technical Meeting, Electrochemical Society of India 1985,
32.
(26) Kalaignan, G. P.; Muralidharan, V. S.; Vasu, K. I. Proceedings
of the Annual Technical Meeting, Electrochemical Society of India 1985,
32.
1978, 24, 21.

(24) Jayalakshmi, N.; Muralidharan, V. S. J. Power Sources 1990,
32, 341.
evolution takes place with the discharge of $\text{K}^+$ ions as follows:\(^{28}\)

$$\text{K}^+ + \text{e}^- \rightarrow \text{K(S)}$$

$$\text{K(S)} + \text{H}_2\text{O} \rightarrow \text{K}^+ + \text{S} + \text{H}_{\text{ads}} + \text{OH}^-$$

$$2\text{H}_{\text{ads}} \rightarrow \text{H}_2$$

where $\text{S}$ is the oxide surface site. In neutral solutions employed in the present study, hydrogen undergoes the intercalation process instead of the evolution process.

Another interesting result that confirms the above hypothesis was the cyclic voltammograms obtained for LiMn$_2$O$_4$ in KCl solutions at a slow scan rate (Figure 6). Only one set of redox peaks appeared in all the scans. This was understandable because the time window provided to complete the intercalation process was long enough.

Last, to confirm our hypothesis of alkali metal cation intercalation in LiMn$_2$O$_4$, EDX studies of electrochemically treated electrodes were carried out. The PIGE electrode immobilized with LiMn$_2$O$_4$ was cycled in a 0.1 M KCl solution and then subjected to EDX detection. The results showed that the cycled LiMn$_2$O$_4$ electrode contains potassium ions in it. If the replacement of lithium by potassium ions was 100%, then the weight percents of K and Mn should be 26.2 and 73.8, respectively, whereas from the EDX results, we found that the weight percents of K and Mn were 4.05 and 95.95, respectively, indicating that the replacement of lithium by potassium ions was partial.

This type of partial proton insertion was reported for spinel LiMn$_2$O$_4$, and the composition of the cathode material after the first charge/discharge studies was noted to be $\text{H}_{0.35}\text{Li}_{0.7}\text{MnO}_2$. Poor efficiency of the oxidation process was attributed to the irreversible trapping of protons in the oxide lattice.\(^{10}\) This observation is consistent with our present work.

**Conclusions**

Lithium manganate was prepared by a simple low-temperature solution combustion method. This method is highly advantageous over the conventional ones because it is cost- and time-effective. The ICP analysis showed the material to have a composition of Li$_{0.92}$Mn$_2$O$_4$. Electrochemical studies revealed the dual cation insertion/extraction. Potassium ion insertion in LiMn$_2$O$_4$ from a neutral electrolyte solution is reported for the first time. Along with protons, $\text{K}^+$, $\text{Li}^+$ and $\text{NH}_4^+$ ions were intercalated into the lithium manganate structure. EDX results of electrochemically treated samples proved the presence of potassium ions in LiMn$_2$O$_4$. The ion exchange of lithium by potassium remains partial.

**Acknowledgment.** M.J. acknowledges provision of a fellowship from Humboldt Stiftung (AvH) and M.M.R. acknowledges a postdoc fellowship from Deutsche Forschungsgemeinschaft (DFG).

LA0340448

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