



ELSEVIER

Journal of Power Sources 97–98 (2001) 512–514

JOURNAL OF
POWER
SOURCES

www.elsevier.com/locate/jpowersour

Magnesium insertion into $\text{Mg}_{0.5+y}(\text{Fe}_y\text{Ti}_{1-y})_2(\text{PO}_4)_3$

Koji Makino*, Yasushi Katayama, Takashi Miura, Tomiya Kishi

Department of Applied Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3-14-1, Kohoku-ku, Yokohama 223-8522, Japan

Received 23 June 2000; accepted 8 January 2001

Abstract

A series of transition metal phosphates, $\text{Mg}_{0.5+y}(\text{Fe}_y\text{Ti}_{1-y})_2(\text{PO}_4)_3$ (MFTP), modified from $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ (MTP) were prepared by sol-gel method and evaluated as cathode materials for rechargeable magnesium cells. The crystal structure of MFTP at $0 \leq y \leq 0.5$ was identical to that of MTP, while their unit cell volumes were smaller than that of MTP due to introduced Mg^{2+} ions. Electrochemical magnesium insertion into MFTP was found possible as observed for MTP. However, the limiting extent of magnesium insertion into MFTP at $0.1 \leq y \leq 0.5$ was small compared with MTP and remarkably dependent on the current density during discharge, suggesting that the insertion limit is determined not by the number of available sites for Mg^{2+} or electrons but by the mobility of Mg^{2+} in the host varying with the unit cell volume. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Magnesium insertion; NASICON-structure; Sol-gel method; Diffusion control

1. Introduction

The so-called lithium ion cells are now widely accepted as secondary batteries having high energy density. On the other hand, rechargeable magnesium cells may be another candidates of high energy density cells, because the raw material costs may be lower than those in lithium ion cells and magnesium is less dangerous than lithium. However, it has been known that the rate of Mg^{2+} insertion into ion-transfer host is slow owing to the strong polarization of small and divalent Mg^{2+} ion compared to Li^+ or Na^+ [1–5].

Lithium and sodium ions can be inserted/extracted reversibly into/from a series of compounds having a general formula of $\text{A}_x\text{M}_2(\text{XO}_4)_3$ ($\text{A} = \text{Li}$ or Na ; $\text{M} =$ transition metal; $\text{X} = \text{S}$, P or As) [6,7], derived from well-known fast ionic conductor of NASICON [8], because they have large enough interstitial voids to uptake guest species and high structural stability of three-dimensional framework. Consequently, fast Mg^{2+} transport may also be expected in such compounds.

In this study, NASICON-structured $\text{Mg}_{0.5+y}(\text{Fe}_y\text{Ti}_{1-y})_2(\text{PO}_4)_3$ (MFTP), modified from $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ (MTP), are prepared by sol-gel method and investigated as a magnesium host.

2. Experimental

2.1. Preparation of $\text{Mg}_{0.5+y}(\text{Fe}_y\text{Ti}_{1-y})_2(\text{PO}_4)_3$

An amount of 0.1 mol dm^{-3} $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (Wako Chemicals, >99%) and 0.1 mol dm^{-3} $\text{NH}_4\text{H}_2\text{PO}_4$ (Wako Chemicals, >99%) aqueous solutions were prepared separately, in addition to 0.1 mol dm^{-3} FeCl_3 (Wako Chemicals, >95%) and 0.1 mol dm^{-3} $\text{C}_4\text{H}_9\text{O}[\text{Ti}(\text{OC}_4\text{H}_9)_2\text{O}]_4$ C_4H_9 (Wako Chemicals, >95%) ethanol solutions. These solutions were mixed at the calculated ratio to give $\text{Mg}_{0.5+y}(\text{Fe}_y\text{Ti}_{1-y})_2(\text{PO}_4)_3$. The obtained sol solution was further stirred at 70°C for 6 h to form a gel, which was dried at 90°C for 12 h to give a powder. The powder was heated at 300 and then 500°C to remove ammonium and acetate groups, followed by final firing at 700°C for 24 h.

2.2. Electrochemical measurements

Electrochemical magnesium insertion from 1 mol dm^{-3} $\text{Mg}(\text{ClO}_4)_2$ /propylene carbonate (PC) solution was performed in a cylindrical glass cell. The sample electrode pellet was prepared by pressing the mixture of MFTP (or MTP), acetylene black (Denka black, Denkakagaku Kogyo) and PTFE (Mitsui-Du Pont) at 70:25:5 in wt.% under a pressure of $2 \times 10^3 \text{ kg cm}^{-2}$ on a porous nickel sheet. Magnesium ribbon was used as the counter electrode. The reference electrode consisted of silver wire immersed in 0.1 mol dm^{-3} AgClO_4/PC solution, which was separated

* Corresponding author.

from the cell electrolyte by a glass filter. All procedures and cell construction were performed under dried argon atmosphere in a glove box.

X-ray diffraction (XRD, Rigaku, RINT-1300) was carried out both before and after electrochemical measurements.

3. Results and discussion

3.1. Preparation of $Mg_{0.5+y}(Fe_yTi_{1-y})_2(PO_4)_3$

When final firing temperature, T_F , was set below 500°C , the sample ($y = 0.5$) was amorphous showing no sharp XRD line. A crystalline MFTP phase could be obtained at $T_F = 700^\circ\text{C}$ and all diffraction lines could be consistent with the simulation data as hexagonal (space group: $R\bar{3}c$). However, TiP_2O_7 and $Mg_2P_2O_7$ phases appeared due to the decomposition of MFTP phase at $T_F = 900^\circ\text{C}$.

A set of samples having nominal composition of $0 \leq y \leq 1.0$ in $Mg_{0.5+y}(Fe_yTi_{1-y})_2(PO_4)_3$ obtained at $T_F = 700^\circ\text{C}$ were investigated by XRD. MTP-structured MFTP could be obtained as single phase only at $0 \leq y \leq 0.5$ without uncertain XRD line. $Mg_3(PO_4)_2$ and $FePO_4$ phases appeared at $0.5 < y$ as the impurity and their XRD intensities increased with increasing y . These results indicate that solid solution region of MFTP phases is at $0 \leq y \leq 0.5$.

The effects of Ti^{4+} substitution with Fe^{3+} on lattice parameters were shown in Fig. 1, where the shrinkage in c -axis occurs due to the relaxed O–O repulsion in $(Fe, Ti)O_6$ octahedra and to the bond formation between introduced excess Mg^{2+} and O in $(Fe, Ti)O_6$ octahedra. On the other hand, a -axis expands to compensate the c -shrinkage in the flexible NASICON-framework [6,9]. However, this compensation seems too little to prevent the decrease in unit cell volume. The unit cell volume decreases remarkably at $0 \leq y \leq 0.1$ then gradually at $0.1 \leq y \leq 0.5$.

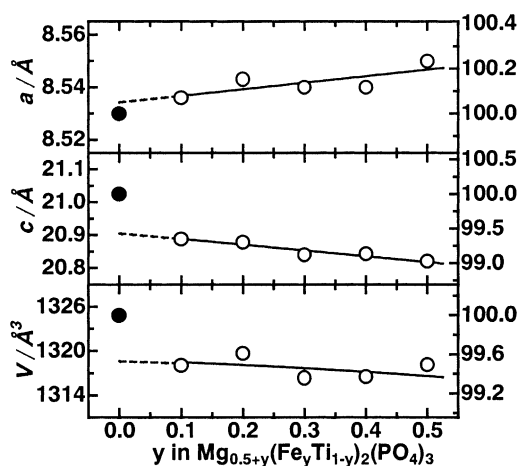


Fig. 1. Unit cell parameters of $Mg_{0.5+y}(Fe_yTi_{1-y})_2(PO_4)_3$.

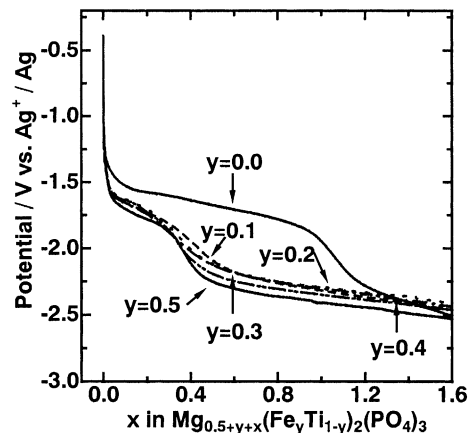


Fig. 2. Discharge curves of $Mg_{0.5+y}(Fe_yTi_{1-y})_2(PO_4)_3$ at $-50 \mu\text{A cm}^{-2}$.

3.2. Electrochemical magnesium insertion

Galvanostatic discharge curves ($-50 \mu\text{A cm}^{-2}$ based on apparent geometrical area) of MFTP ($y = 0.1-0.5$) and MTP are compared in Fig. 2. For MTP the potential plateau at about -1.6 V (versus Ag^+/Ag) continues up to $x = 1.0$, the limit of electronic sites given by Ti^{4+}/Ti^{3+} , where x denotes the calculated amount of inserted Mg^{2+} per formulae. For MFTP ($y = 0.1-0.5$) a similar plateau can be observed, although its length is $x < 0.5$ independent of y . At the final stage of $x = 1.2$, both MFTP and MTP show substantially identical discharge potential below -2.4 V , where an unexpected reaction such as solvent decomposition might occur. These results may suggest that the insertion limit for MFTP is determined not by the number of available sites for Mg^{2+} or electrons but by a kinetic factor, probably the mobility of Mg^{2+} in the host lattice.

A preliminary XRD study after discharge shows that magnesium insertion can proceed topotactically into both MFTP ($y = 0.5$) and MTP, where the unit cell parameters remain almost constant at various stages of magnesium

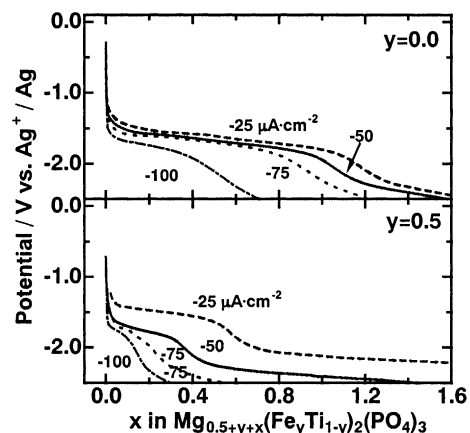


Fig. 3. Discharge curves of $Mg_{0.5+y}(Fe_yTi_{1-y})_2(PO_4)_3$ at various current densities.

insertion up to $x = 1.0$. Mg^{2+} may possibly be accommodated in this host without any phase transition, because NASICON-lattice have large cationic sites and the flexible structure.

Effects of current densities on discharge curves of MFTP ($y = 0.5$) and MTP are shown in Fig. 3, where both the potential and length of discharge plateau are rate-dependent markedly for MFTP ($y = 0.5$) compared with MTP. Moreover, the proportional relationship between the square root of x and the inverse of current densities (applying at $\geq |-50 \mu\text{A cm}^{-2}|$ for MFTP; $\leq |-75 \mu\text{A cm}^{-2}|$ for MTP) suggests that the insertion limit is controlled by the diffusion process.

4. Conclusion

MFTP samples having MTP-lattice could be obtained at $0 \leq y \leq 0.5$, and their unit cell volume was smaller than that of MTP by ca. 0.8% owing to the c -shrinkage caused by introduced Mg^{2+} ions. Electrochemical magnesium insertion

into MFTP was found possible as into MTP. However, the insertion limit was smaller for MFTP than $x = 1.0$ for MTP and decreased with increasing discharge rate, suggesting that the insertion is under kinetic control of Mg^{2+} diffusion in the MFTP host.

References

- [1] P. Novák, W. Scheifele, O. Haas, J. Power Sources 54 (1995) 479.
- [2] T.D. Gregory, R.J. Hoffman, R.C. Winterton, J. Electrochem. Soc. 137 (1990) 775.
- [3] M.E. Spahr, P. Novák, O. Haas, R. Nesper, J. Power Sources 54 (1995) 346.
- [4] P. Novák, W. Scheifele, F. Joho, O. Haas, J. Power Sources 142 (1995) 2544.
- [5] P. Novák, J. Desilvestro, J. Electrochem. Soc. 140 (1993) 140.
- [6] C. Delmas, A. Nadiri, Solid State Ionics 28 (1988) 419.
- [7] C. Delmas, F. Cherkaoui, A. Nadiri, P. Hagemuller, Mater. Res. Bull. 22 (1987) 631.
- [8] J.B. Goodenough, H.Y.P. Hong, J.A. Kafalas, Mater. Res. Bull. 11 (1976) 203.
- [9] O. Mentre, F. Abraham, Solid State Ionics 72 (1994) 293.