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Redox reactions in condensed oxide systems XIII: Li insertion reaction of $MgTiO_3$ and the spinels Mg_2TiO_4, $MgNiMnO_4$ and MMn_2O_4 (M ≡ Mn, Mg, Ni)

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Zusammenfassung

Es wird über den Einbau von Lithium in $MgTiO_3$, Mg_2TiO_4 und die Spinelle MMn_2O_4 (M ≡ Mn, Mg, Ni) sowie $MgNiMnO_4$ durch Umsetzung mit *n*-BuLi in Heptan berichtet. Die Bedingungen zur Erreichung definierter Endstufen der Reaktion werden am Beispiel des Systems $Li_xMn_3O_4$ ermittelt. Nur die Verwendung hoch disperser Pulver ergibt für $MgTiO_3$ und Mg_2TiO_4 eine Umsetzung. Die erhaltenen Verbindungen $LiTi_4Mg_4O_{12}$ und $LiMg_4Ti_2O_8$ sind unbeständig an Luft. Sie werden röntgenographisch und durch magnetische Messungen charakterisiert. Die Befunde an den Mn-Spinellen werden im Vergleich mit Angaben der Literatur diskutiert.

Abstract

Lithium insertion reactions are reported utilizing n-BuLi dissolved in heptane applied to $MgTiO_3$, Mg_2TiO_4 and to the spinel-type compounds MMn_2O_4 (M ≡ Mn, Mg, Ni) and $MgNiMnO_4$. The system $Li_xMn_3O_4$ is studied as an example in order to reveal the optimum conditions for achieving definite final product stages. The lithium insertion reaction of $MgTiO_3$ and Mg_2TiO_4 is bound to the application of highly disperse powders as a prerequisite. The compounds $LiTi_4Mg_4O_{12}$ and $LiMg_4Ti_2O_8$ are unstable in air. Characterization has been accomplished by X-ray diffraction and magnetic measurements. The results observed for the spinels MMn_2O_4 (M ≡ Mn, Mg, Li) and $MgNiMnO_4$ are discussed in comparison with data reported in the literature.

1. Introduction

Topotactic lithium insertion and extraction at low temperatures in a variety of spinel phases including Fe_3O_4 [1], Mn_3O_4 [2], Co_3O_4 [3, 4], $LiMn_2O_4$ [2, 3, 5, 6] $M^{II}Fe_2O_4$ (M^{II} ≡ Mn, Fe, Co, Ni, Cu, Zn, Cd) [7], ZnB_2O_4 (B^{III} ≡ Co, Cr, Fe–Mn) [8] and $LiFe_5O_8$, $Li_2FeMn_3O_8$ and $Li_2ZnMn_3O_8$ [9] have demonstrated fast Li^+ ion diffusion. The ease of the reducibility of the transition metal cations was shown to be an important factor in the extent of lithium insertion reactions of spinels. On the other hand, $LiTi_2O_4$ is also able to become intercalated as a result of interaction with *n*-BuLi [10]. Relations

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between the structure and Li^+ ion mobility of lithium insertion compounds have been reviewed by several authors [11–14].

Comparatively little information has been reported on the preparation conditions where the lithium insertion is considered as kinetically dependent on time. Different final stages seem to be achieved, influenced by the reactivity of the solid component taking part in the insertion reaction. Appropriate mixtures of 2-ethoxi-ethoxides of magnesium and titanium were shown to yield $MgTiO_3$ and Mg_2TiO_4 in a highly disperse state with increased sintering activity [15]. Substitution of magnesium for lithium in the series $Mg_xLi_{1-x}Ti_2O_4$ was studied in an earlier paper [16]. In order to evaluate the ability of $MgTiO_3$ and Mg_2TiO_4 to become reduced by lithium insertion the behaviour of Mn_3O_4 in contact with n-BuLi has also been studied. Moreover, the investigations are extended to $MgMn_2O_4$, $NiMn_2O_4$ and $MgNiMnO_4$.

2. Experimental details

2.1. *Preparation*

Mn_3O_4 prepared from $MnCO_3$ by ignition at 970 °C in air yielding a specific surface area of 0.4 m^2 g^{-1} has been brought into contact with a solution of n-BuLi in heptane (about 0.3 mol l^{-1}) utilizing a molar ratio Mn_3O_4:*n*-BuLi = 1:2. The solution of *n*-BuLi which has to be free of LiCl was obtained following the preparation route as described in ref. 17. The progress of the reaction

$$Mn^{II}Mn_2^{III}O_4 + xLiC_4H_9 \longrightarrow Li_xMn_{1+x}^{II}Mn_{2-x}^{III}O_4 + \frac{x}{2}C_8H_{18} \qquad (1)$$

was controlled for different conditions: (a) shaking the suspension at room temperature in a closed vessel; (b) shaking it at room temperature together with vitreous spheres in order to remove the product layer covering the surface; (c) keeping it at 70 °C without stirring; and (d) applying ultrasound (40 kHz, about 0.15 W cm^{-2}) at 45 °C.

Aliquots have been taken away at definite times, carefully avoiding access of moisture or oxygen, to determine the content of unconsumed *n*-BuLi acidimetrically. Decreasing the *n*-BuLi concentration in the solution gives a measure for the increasing lithiazation of the solid compound at the bottom of the closed vessel. Within the first few hours the dark-red colour of Mn_3O_4 changes to black. After about 40 h application of ultrasound at the conditions labelled (d) above a final value of x was achieved with sufficient reproducibility according to eqn. (1).

No visible reaction is observed between *n*-BuLi dissolved in heptane and $MgTiO_3$ or Mg_2TiO_4 resulting from conventional preparation: high temperature treatment of $MgO–TiO_2$ or $2MgO–TiO_2$ pellets at 1400 °C, grinding and repeating the procedure. The powders do not show any reactivity in contact with *n*-BuLi. On the other hand, hydrolyses of mixtures of $Mg(OCH_2CH_2OC_2H_5)_2$ and $Ti(OCH_2CH_2OC_2H_5)_4$ in the molar ratio 1:1 or 2:1 dissolved in 2-ethoxyethanol provides highly disperse powders. After evaporation and calcination of the residue by heating to 700 °C (3 h), specific surface areas of 16 $m^2 g^{-1}$ for $MgTiO_3$ and of 43 $m^2 g^{-1}$ for Mg_2TiO_4 are obtained [15]. The powders still show a small ignition loss of 1.3%. Starting from these powder states the reactions

$$MgTiO_3 + xLiC_4H_9 \longrightarrow Li_xMgTi^{III}_xTi^{IV}_{1-x}O_3 + \frac{x}{2}\,C_8H_{18} \tag{2}$$

$$Mg_2TiO_4 + xLiC_4H_9 \longrightarrow Li_xMg_2Ti^{III}_xTi_{1-x}O_4 + \frac{x}{2}\,C_8H_{18} \tag{3}$$

take place relatively fast if ultrasound and increased temperature are applied. A blue colour appears immediately after covering the powders with the solution of heptane containing n-BuLi in sufficient excess. Keeping the vessel closed during the whole reaction time, final x values were achieved after 40–70 h ultrasound treatment at 70 °C. Presumably, because of lowering of the specific surface area to 2 $m^2 g^{-1}$, the reactivity is lost when the powders are heated to 1100 °C for 1 h. Even after prolonged reaction times x values of only 0.01 have been obtained.

$NiMn_2O_4$ was prepared following the oxalate precursor route as described earlier [18]. Starting from oxalate mixed crystals $MgNiMnO_4$ has been also successfully prepared [19]. $MgMn_2O_4$ was obtained by calcination of a mixture of manganese carbonate with MgO (mole ratio 1:2) at 600 °C, pelletization of the powder and keeping it at 1000 °C for 24 h. Insertion experiments have been accomplished utilizing a 2.5 M solution of n-BuLi in heptane with application of ultrasound at 45 °C for various times:

$$NiMn_2O_4 + xLiC_4H_9 \longrightarrow Li_xNiMn^{II}_xMn^{III}_{2-x}O_4 \tag{4}$$

$$MgNiMnO_4 + xLiC_4H_9 \longrightarrow Li_xMgNiMn^{III}_xMn^{IV}_{1-x}O_4 \tag{5a}$$

$$LiMgNiMn^{III}O_4 + xLiC_4H_9 \longrightarrow Li_{1+x}MgNiMn^{II}_xMn^{III}_{1-x}O_4 \tag{5b}$$

$$MgMn_2O_4 + xLiC_4H_9 \longrightarrow Li_xMgMn^{II}_xMn^{III}_{2-x}O_4 \tag{6}$$

2.2. *Analyses*

In order to elaborate the optimum conditions for lithium insertion the reaction of eqn. (1) has been studied by taking away aliquots of the n-BuLi solution for acidimetric lithium titration after definite times. The difference from the initial concentration of n-BuLi has to be equal to the lithium content absorbed by the weighing-out loss of Mn_3O_4. The values x_{ac} determined were found to be in accordance with lithium analyses of the solids carried out by atomic absorption spectrometrie (AAS). Different reaction times without intermediate opening of the vessel have been applied for the reactions (2)–(6) in order to avoid falsification by uncontrolled access of traces of moisture, oxygen or carbon dioxide.

As a second method for analytical characterization of the products the content of Mn^{III} and Mn^{IV} has been determined by dissolution of a weighing-out loss of the substances in diluted hydrochloric acid containing a definite concentration of Fe^{II} and titration with 0.1 M Ce^{IV} solution. The procedure already described in detail earlier [20] allows us to determine the remaining content of oxidation equivalents of manganese, which is related to the inserted lithium as indicated by the formulas of eqns. (1) and (4)–(6). The method is also applicable to the Ti^{III}-containing compounds, because the Fe^{II} formed by the reduction of Fe^{III} may be determined by titration with the 0.1 Ce^{IV} solution. Besides, the reaction

$$6Ti^{III} + Cr_2O_7^{2-} + 14H^+ \rightleftharpoons 6Ti^{IV} + 2Cr^{III} + 7H_2O \qquad (7)$$

was applied for measuring the reduction equivalents formed in $MgTiO_3$ and Mg_2TiO_4 as a result of lithium insertion according to eqns. (2) and (3). The independent determination of the compositional parameter x_{ox} by redox titration allows comparison with the values x_{ac} obtained acidimetrically.

Finally, the total content of manganese or titanium has been separately determined. The results allow comparison with the data calculated from the formulae which are deduced from the average values x.

2.3. *X-ray diffraction measurements*

The products of preparation were found to be unstable in air. Therefore X-ray diffraction measurements required careful transfer into the capillary tube; Cu Kα irradiation has been applied. Generally, the reflexes appear broadened. Obviously, because of the action of ultrasound, particle size becomes significantly decreased. Drastic decrease of the average particle size of inorganic solids without achieving amorphization is shown to be generated by the action of high intensity ultrasound (20 kHz, 20 W cm^{-2}) within comparatively short times (about 2 h) [21]. In spite of the longer treatment the very much lower ultrasound intensity applied in the investigations presented allows us to assume that the main part of the substance is still in the crystalline state.

2.4. *Magnetic measurements*

The magnetic properties of the Ti^{III}-containing compounds (paramagnetic at room temperature, yielding μ_{exp}) have been obtained by measuring the magnetic susceptibility with the Gouy method. The data were compared with the values μ_{eff} calculated utilizing the magnetic moment for Ti^{III} ($\mu_{eff} = 1.7–1.8$ μ_B) from data in the literature [22]. (μ_B denotes the Bohr magneton.)

3. Results and discussion

The results of acidimetric titration concerning the lithium insertion reaction of Mn_3O_4 based on eqn. (1) are shown in Fig. 1. The analytical data of the final composition are collected in Table 1. The low reproducibility for application of the conditions labelled (a) above is indicated. Obviously, the conditions (b) involving the presence of vitreous spheres during shaking

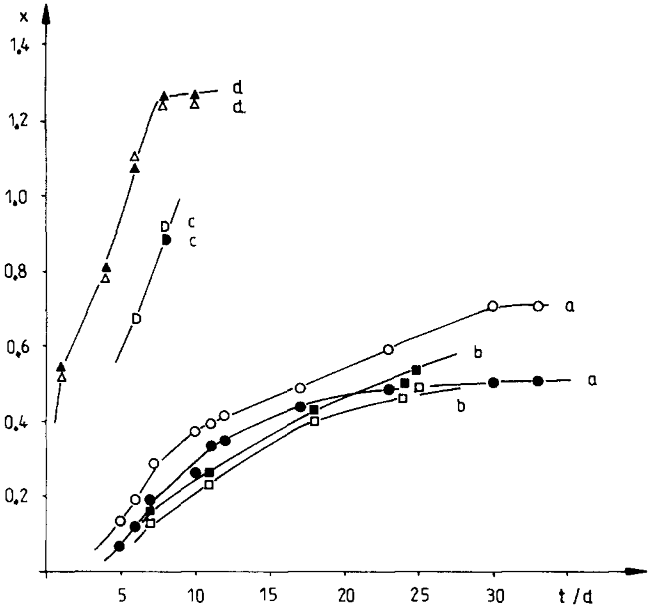

Fig. 1. Acidimetrically determined insertion of lithium in Mn_3O_4 in contact with *n*-BuLi dissolved in heptane under various conditions: a, shaking at room temperature; curves b, shaking at room temperature together with vitreous spheres; curve c, keeping at 70 °C; curve d, applying ultrasound at 45 °C.

at room temperature lead to removal of the surfaces and therefore the two curves are coming closer together. Increasing the temperature accelerates the reaction rate significantly, which is shown by curves c and d. Saturation at $x = 1.25$ is achieved at 70 °C after 8 days under the action of ultrasound of comparatively low intensity. The compound $Li_{1.25}Mn_3O_4$ or $Li_5Mn_{12}O_{16}$ is obtained. Thackeray *et al.* [2] achieved a value $x = 1.20$ after 72 at 50 °C without application of ultrasound. The X-ray diffraction pattern is in accordance with data published for $LiMn_3O_4$ [2]. Because of the reduction of one-half of Mn^{III} and as a result of a cooperative displacement of the A-site Mn^{II} ions to B sites the tetragonally distorted spinel structure of Mn_3O_4 ($c/a = 1.16$) becomes transformed into a sodium chloride type of structure of reduced tetragonal distortion ($c/a = 1.05$) [23]. $LiMn_3O_4$ is unstable in air. The corresponding curve in Fig. 2 refers to hydrolysis and contamination by water, oxygen and carbon dioxide.

The reaction of $MgTiO_3$ with *n*-BuLi under comparable conditions provides $Li_{0.25}MgTiO_3$ or $Li_3Mg_{12}Ti_{12}O_{36}$ (Table 1) respectively, *i.e.* at the conditions applied the six-layer ilmenite-type structure with $a_0 = 505.3$ pm, $c_0 = 1389.7$ pm and six $MgTiO_3$ formula units in the elementary cell indicates the ability to contaminate with preferably three Li^+ ions in the volume of two cells. At the same time three Ti^{III} atoms are formed. X-ray diffraction measurements imply an unchanged structure. The behaviour of the ignited $MgTiO_3$ samples with the lower specific surface area shows that the state of highly reactive

TABLE 1

Analytical data of the products of lithium insertion reactions of various spinels and $MgTiO_3$[a]

Compound	x_{ac}	x_{ox}	$\bar{x}$	Mn, Ti(%)	
				Calculated	Experimental
$Li_xMn^{II}_{1+x}Mn^{III}_{2-x}O_4$	1.25	1.30	1.25	69.4	68.6
(US, 45 °C, 50 h)[b]		1.29			
		1.19			
		1.20			
$Li_xMgTi^{III}_xTi^{IV}_{1-x}O_3$	0.24	0.26	0.25	39.3	39.3
(US, 70 °C, 90 h)		0.27			
	0.23	0.26	0.25	39.3	39.1
		0.27			
$Li_xMg_2Ti^{III}_xTi^{IV}_{1-x}O_4$	0.46	0.44	0.45	29.3	29.3
(US, 70 °C, 90 h)		0.44			
	0.44	0.43	0.44	29.3	29.3
		0.44			
$Li_xNiMn^{II}_xMn^{III}_{2-x}O_4$	1.19	1.17	1.18	45.6	–
(US, 70 °C, 50 h)		1.18			
	1.24	1.19			
		1.19			
(US, 45 °C, 120 h)	–	2.00	2.00	44.6	–
		2.00			
$Li_xNiMgMnO_4$	–	1.21	1.19	26.1	–
(US, 45 °C, 50 h)		1.21			
		1.17			
		1.17			
$Li_xMgMn_2O_4$	–	1.00	1.00	53.6	
(US, 45 °C, 120 h)		1.00			
(US, 45 °C, 180 h)	–	1.25	1.25	53.1	–
		1.25			

[a] Utilizing *n*-BuLi dissolved in heptane.

[b] Preparation conditions; US, ultrasound.

$MgTiO_3$ is absolutely necessary for successful lithium insertion. The dark-blue compound is unstable in contact with air. Efforts to prepare tablets by pressure densification and sintering of the powder for conductivity measurements failed.

In accordance with expectation $Li_{0.25}MgTi^{III}_{0.25}Ti^{IV}_{0.75}O_3$ is paramagnetic with a susceptibility of $\chi_{mol} = 20.12 \times 10^{-6}$ cm^3 mol^{-1} at 294 K. For diamagnetic correction the data in Table 2 have been taken into account, yielding a correction term of $\chi_{dia} = -45.15 \times 10^{-6}$ cm^3 mol^{-1}. From the calculation of $\mu_{eff} = 2.84(\chi_{mol} - \chi_{dia})^{1/2}$ the value $\mu_{eff} = 0.393$ μ_B is obtained. Assuming spin-only magnetic behaviour the presence of $x_{magn} = 0.23$ electrons is deduced, which is in sufficient agreement with the analytical data of Table 1. The results of magnetic measurements convincingly imply single electrons localized

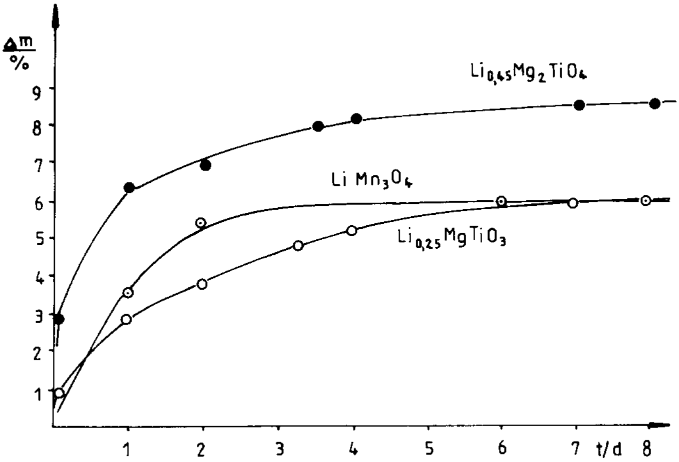

Fig. 2. Increase of the weight of samples in contact with air at room temperature, showing decomposition of the compounds.

TABLE 2

Corrections for diamagnetism

Ion	Correction ($cm^3\ mol^{-1}$)
Li^+	-0.6×10^{-6}
Mg^{II}	-3.0×10^{-6}
Ti^{III}	$+9\times10^{-6}$
Ti^{IV}	$+5\times10^{-6}$
O^{2-}	$+12\times10^{-6}$

in the form of Ti^{III} atoms without indication of spin compensation. Thus the conductivity is assumed to be small. On the other hand, high conductivity values and reduced paramagnetism interpreted by spin interaction has been observed in the solid solution series $MgTiO_3$–Ti_2O_3 or $Mg_{1-x}Ti^{IV}_{1-x}Ti^{III}_{2x}O_3$ respectively [24–26].

$Li_{0.45}Mg_2Ti^{III}_{0.45}Ti^{IV}_{0.55}O_4$ as the final stage composition of the lithium insertion reaction of Mg_2TiO_4 — the approach is presumably via $Li_{0.5}Mg_2TiO_4$ or $LiMg_4Ti_2O_8$ — is also a dark-violet substance. The X-ray diffraction pattern shows that the scattering reflexes of the cubic structure of the inverted spinel $Mg(MgTi)O_4$ ($a_0 = 844.09$ pm) with random distribution of the Mg^{II} and Ti^{IV} atoms on the B sites remains unchanged. Within a few days the compound becomes decomposed in contact with air (Fig. 2). The paramagnetic susceptibility at 294 K is given by $\chi_{mol} = 100.15\ cm^3\ mol^{-1}$, yielding $\mu_{eff} = 0.618$ μ_B which corresponds to $x_{magn} = 0.36$. This value is a little smaller than x_{ac} and x_{ox} of Table 1.

The results of the lithium insertion reactions of $NiMn_2O_4$ are also summarized in Table 1, indicating that ultrasound treatment for a rather long period allows us to attain the composition $Li_2NiMn^{II}O_4$. The X-ray diffraction pattern shows only three sufficiently intensive rather broadened but distinct reflexes at $\vartheta = 17.3°$, 21.05° and 31.2°. They are consistent with a cubic elementary cell with $a_0 = 429 \pm 2$ pm. The lattice parameter of $NiMn_2O_4$ is given by $a_0 = 837.8$ pm. Both diagrams appear superimposed in the X-ray diffraction pattern of $Li_{1.18}NiMn_2O_4$ obtained after a reduced reaction time. Chen *et al.* [8] also studied the lithium insertion reaction of $NiMn_2O_4$ utilizing n-BuLi in heptane. They obtained $Li_{1.8}NiMn_2O_4$ after 10 days at room temperature without the influence of ultrasound. The product was found to be a heterogeneous mixed phase.

The cubic spinel $MgNiMnO_4$ ($a_0 = 833.2$ pm) [19] contaminates lithium from n-BuLi dissolved in heptane up to about $x = 1.2$. Besides the occurrence of the unchanged X-ray diffraction pattern of $MgNiMnO_4$, six weak reflexes are additionally observed in the pattern of $Li_{1.2}MgNiMn_2O_4$: $\vartheta = 10.70°$, 15.99°, 16.80°, 19.60°, 24.60° and 33.00°. Hitherto indexing has failed.

In contact with dissolved n-BuLi, $MgMn_2O_4$ existing predominantly in a normal spinel-type construction takes lithium inserts up to a similar degree to $MgNiMnO_4$ which is of the inverse type. X-ray diffraction measurements reveal a change from $a_0 = 810.1$ pm and $c_0 = 934.6$ pm for $MgMn_2O_4$ ($c/a = 1.154$) [27] to $a_0 = 829 \pm 8$ pm and $c_0 = 930 \pm 10$ pm ($c/a = 1.11$) for $Li_{1.25}MgMn_2O_4$. Obviously, as for $Li_xMn_3O_4$ the Li^+ ions are incorporated on octahedral sites accompanied by site changing of Mg^{II} or Mn^{II} from the A to the B sites of the spinel structure (Mn_3O_4: $c/a = 1.16$; $LiMn_3O_4$: $c/a = 1.05$) [2, 23]. The results are in accordance with the behaviour of $ZnMn_2O_4$ and $CdMn_2O_4$ submitted to lithium insertion as shown in the literature [8].

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