A Study of the Na$_x$TiO$_2$ System by Electrochemical Deintercalation

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Abstract. The electrochemical deintercalation from the sheet oxide NaTiO$_2$ leads to new Na$_x$TiO$_2$ materials. The deintercalation is reversible over the range $0.70 \lesssim x \leq 1$, whereas irreversible modifications of the host structure occur by overvoltage ($x \lesssim 0.70$). This behavior, which can be explained by migration of some titanium ions from the slabs to the intersheet space, may be considered as a 2D → 3D structural transition.

1. Introduction

Some of us have recently reported studies of Na$_x$MO$_2$ systems (M = Cr, Ni, Co) by electrochemical deintercalation from NaMO$_2$ sheet oxides [1, 2]. These investigations have shown the possibility of the synthesis of new metastable phases at room temperature. Structural transitions between sheet structures can occur so far as they differ only by sheet gliding.
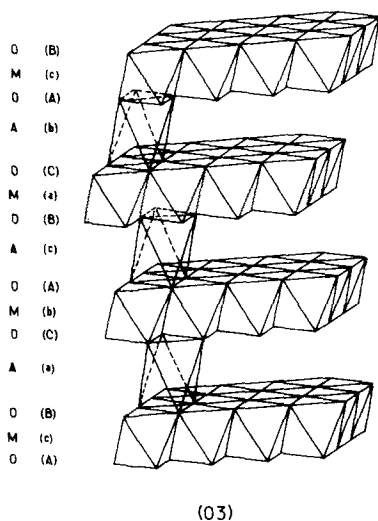

Fig. 1.   Sheet structure of NaTiO$_2$(O3).

In all those systems, a rapid voltage increase of Na/Na_xMO_2 cells is observed for a relatively small deintercalation range. For $x \simeq 0.80$, the potential already attains the upper stability limit of the propylene carbonate used as solvent in the liquid electrolyte (about 3.5 V vs sodium). This behavior has been ascribed to the very high oxidizing character of tetravalent chromium, cobalt or nickel. As a consequence, it is difficult to obtain more deintercalated phases.

In an attempt to decrease the voltage of such cells and to achieve a corresponding increase in their deintercalation capacity, we have studied Na_xMO_2 phases where M has a more stable tetravalent state. In this paper, an electrochemical study using $NaTiO_2$ as the starting material is reported. As with other $NaMO_2$ oxides (M = $3d$ element), $NaTiO_2$ has a layer structure (Figure 1) [3]. Sodium is intercalated between MO_2 slabs composed of edge-sharing MO_6 octahedra and has an octahedral environment. According to a previously described notation, this structure is symbolized by O3 [4].

It should be noted that layer-type Na_xTiO_2 bronzes have never been previously reported. Nevertheless, a Na_xTiO_2 bronze ($x \simeq 0.20$) is well-known, but this material has a three-dimensional skeleton structure [5].

2. Experimental

2.1. STARTING MATERIALS

$NaTiO_2$ was prepared for the first time by Onillon $et\ al.$ [3]. These authors showed that, as the free energy of the reaction $Na + TiO_2 \leftrightarrows NaTiO_2$ is small, a sodium pressure is necessary to shift the equilibrium to the right and $NaTiO_2$ has been obtained here using this method.

A mixture of TiO_2 and an excess of sodium metal (10%) is placed in a nickel sealed tube, which is then placed in a sealed silica tube to avoid further oxidation. The mixture is heated at 400 °C for 10 h and, finally, overnight at 920 °C. Between the two thermal treatments, the material was ground and the excess sodium removed by vacuum distillation (400 °C, 10^{-5} torr). Under such conditions, pure $NaTiO_2$ is obtained as a black powder. It has a very strong
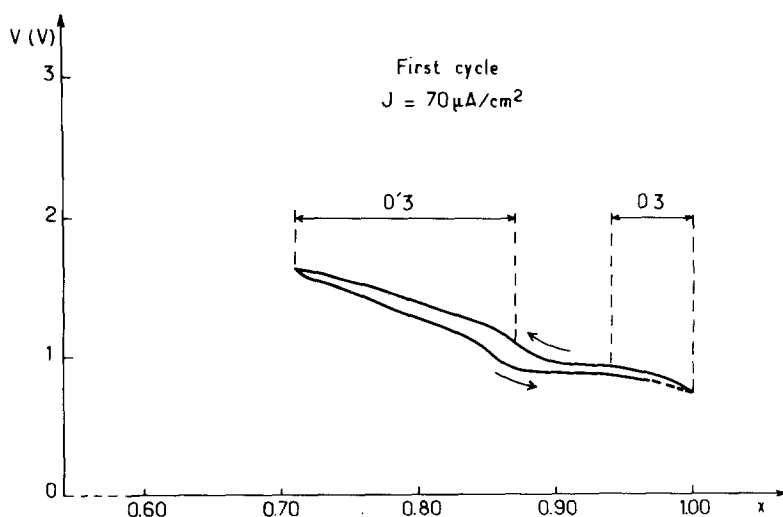
Fig. 2. E.m.f.–composition curve obtained from $NaTiO_2$ (cut off charge voltage 1.6 V).

reducing character and must be kept under an inert atmosphere. Its X-ray diffraction pattern agrees with that previously reported [3].

2.2. ELECTROCHEMICAL STUDY

The electrochemical behavior of $NaTiO_2$ has been studied in cells using a sodium anode, a solution of $NaClO_4$ in propylene carbonate as the electrolyte and $NaTiO_2$ as the cathode. The experimental conditions of building and testing these cells and recovering the cathodic material have been described elsewhere [1]. Since the starting material ($NaTiO_2$) corresponds to a completely discharged phase, the study always began with a charging stage.

The e.m.f. *vs* composition curves obtained for the first cycle are shown in Figures 2–4 for
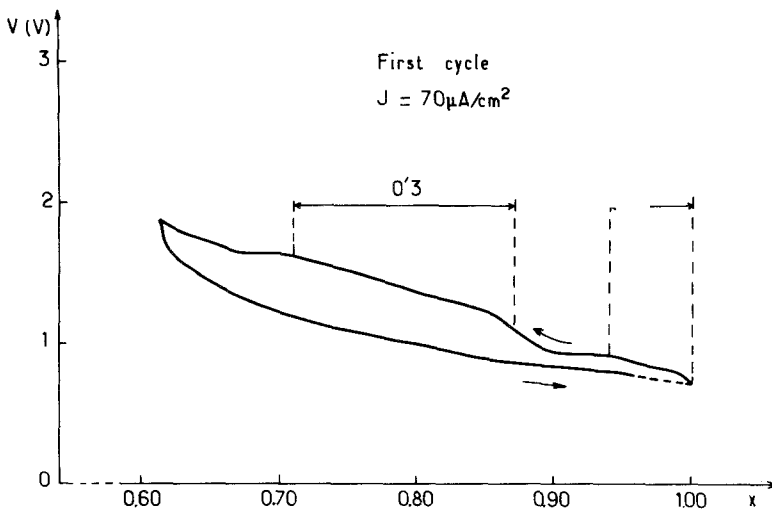

Fig. 3. E.m.f.–composition curve obtained from $NaTiO_2$ (cut off charge voltage 1.9 V).
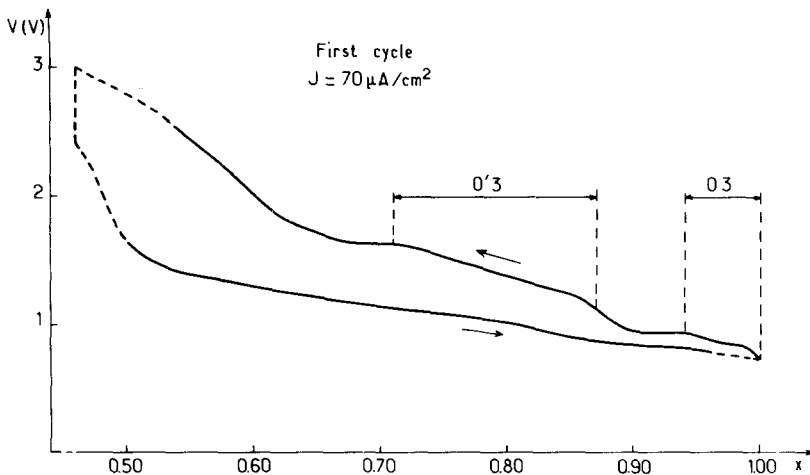

Fig. 4. E.m.f.–composition curve obtained from $NaTiO_2$ (cut off charge voltage 3 V).

an increasing charge depth. The comparison of the discharge curves shows that reversible behavior is observed only if the cell is cycled over a $0.7 \lesssim x \leq 1$ range. If during the charge, the deintercalation rate $(1 - x) \simeq 0.30$ is exceeded, irreversible modifications of the cathodic material occur and the shape of the subsequent voltage vs the composition discharge curve is completely altered.

3. Results and Discussion

As shown in Figures 2–4, nonstoichiometric layer titanium oxides have been obtained for the first time. An examination of Figure 2 shows the small potential values (vs metallic sodium) observed in the Na_xTiO_2 system (0.8–1.6 V). This behavior is attributed to the strong reducing character of trivalent titanium and the potential values must be compared to the Na_xMO_2 (M = Cr, Co, Ni) ones: in those systems, the cell voltage lies in the 2.0–3.5 V range due to the strong oxidizing character of the M^{4+} cations.

$NaTiO_2$ reduces so that a slow reduction of the liquid electrolyte occurs for the lower potential values. Consequently, it is impossible to come back exactly to the composition $NaTiO_2$ during discharge. The corresponding parts of the potential–composition curves are represented by dotted lines in Figures 2–4. This reaction with the liquid electrolyte can lead to a small shift of the composition limit.

3.1. REVERSIBLE RANGE

At the increasing deintercalation rate, two one-phase domains characterized by a continuous variation of the voltage with x are successively observed. X-ray analysis of the cathodic materials indicates that in the first phase the starting O3 structural type is preserved, while a small monoclinic distortion of this structural type characterizes the stronger sodium-deficient phase. Although Na_xTiO_2(O3) ($0.94 \leq x \leq 1$) crystallizes in the rhombohedral system, the parameters of a monoclinic cell have been given for comparison with that of the O'3-type phase in Table I. The cell parameters of the O'3-type phases vary in the homogeneity range, whereas those of O'3 do not change. A similar behavior had been previously observed during the electrochemical study of the Na_xCrO_2 system [2]. Table II gives the X-ray diffraction pattern of $Na_{0.80}TiO_2$ (O'3).

As previously found for other Na_xMO_2 systems, the intrasheet distances ($a_{hex.}$, $a_{mon.}/\sqrt{3}$ and $b_{mon.}$) decrease during deintercalation, due to the higher oxidation state of titanium, while the intersheet distances ($c_{hex.}/3$, $c_{mon.} \sin\beta$) increase [1, 2]. This behavior is illustrated by Figure 5.

Table I. Cell parameters of O3 and O'3 Na_xTiO_2 phases

	$NaTiO_2$(O3)		$Na_{0.94}TiO_2$(O3)		Na_xTiO_2(O'3) $0.71 \leq x \lesssim 0.87$
	hex.	mon.	hex.	mon.	mon.
a(Å)	3.030	5.248	2.978	5.158	5.157
b(Å)	–	3.030	–	2.978	2.977
c(Å)	16.22	6.441	16.73	6.552	6.652
β(°)	–	122.9	–	121.6	122.4
$c \sin\beta$(Å)	–	5.408	–	5.577	5.617

Table II. X-ray diffraction pattern of Na$_{0.80}$TiO$_2$(O'3)

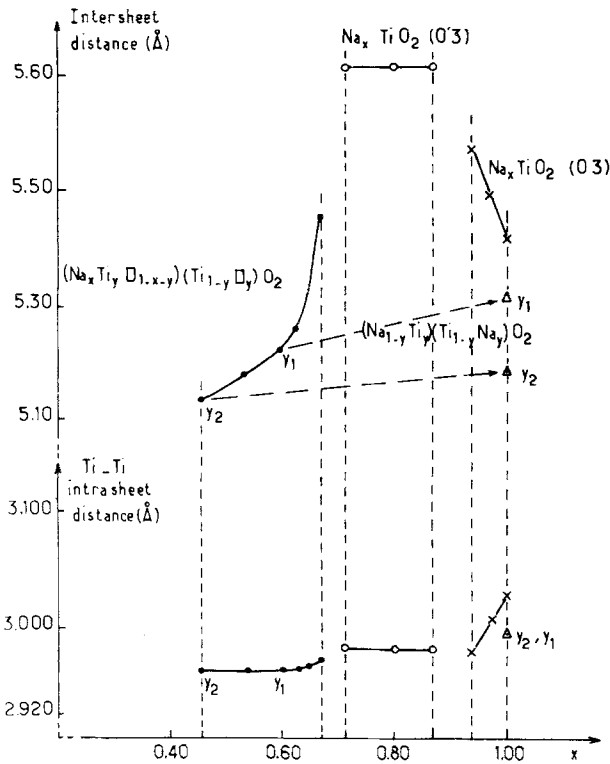| hkl	$d_{obs.}$(Å)	$d_{calc.}$(Å)	$I_{obs.}$
001	5.60	5.61	F
002	2.811	2.808	m
11$\bar{1}$	2.553	2.558	f
110	2.469	2.466	m
11$\bar{2}$	2.202	2.211	TF
111	2.041	2.044	tf
11$\bar{3}$	1.769	1.769	tf
201	1.749	1.755	tf
20$\bar{4}$	1.645	1.651	f
112	1.627	1.627	f
020	1.489	1.489	f
31$\bar{1}$	1.441	1.445	tf
202 004 }	1.406	1.405 1.404 }	tf
310 022 }	1.317	1.316 1.315 }	tf
40$\bar{2}$	1.285	1.284	tf
220	1.233	1.229	tf

Fig. 5. Inter- and intrasheet distances in the Na$_x$TiO$_2$ phases.

3.2. IRREVERSIBLE RANGE

As previously mentioned, if the deintercalation is continued beyond $1 - x \simeq 0.30$, irreversible modifications occur.

The cell resistance increases strongly during charging for $(1 - x) \geq 0.30$. A comparison of charge, discharge and open-circuit-voltage curves shows that the cell polarization is considerably higher during charge than during discharge periods. This behavior agrees with the hypothesis of an irreversible modification of the host structure during the sodium deintercalation, the new form remaining unchanged during the reintercalation. This was corroborated by X-ray analysis. During the deintercalation, a new phase appears for $x \leq 0.67$. The X-ray diffraction patterns can be indexed with a rhombohedral cell. Corresponding hexagonal parameters are listed in Table III. Table IV gives the X-ray diffraction pattern of $Na_{0.46}TiO_2$. The indexations agree with an ABCABC oxygen packing, as in $NaTiO_2$, but the intensities of the diffraction lines are considerably modified. Furthermore, as shown in Figure 5, the intersheet distance (one third of parameter c) decreases rapidly for increasingly charged phases, while it increases slightly during the following sodium reintercalation. As mentioned above, in all reversible Na_xMO_2 systems, the intersheet distances always increase during deintercalation [1, 2] (Figure 5). The observed variation seems to imply a modification of the cationic distribution during overcharging.

From all these data we have made the assumption that the Na_xTiO_2 sheet structures become unstable for a smaller sodium content.

For the limiting composition of the reversible domain ($x \simeq 0.70$), the cell e.m.f. (1.6 V) is usually smaller than the upper stability limit of the electrolyte (about 3.5 V). Consequently, if the cell is overcharged, the Na^+ ions must be removed. To stabilize the structure, some titanium ions may move from the TiO_2 sheet to the intersheet space through a triangular

Table III. Cell parameters of a Na_xTiO_2 solid solution formed by overcharge ($0.46 \lesssim x \lesssim 0.67$).

x	$a(\text{Å})$	$c(\text{Å})$
0.67	2.967	16.41
0.63	2.960	15.78
0.60	2.960	15.66
0.46	2.958	15.41

Table IV. X-ray diffraction pattern of $Na_{0.46}TiO_2$

hkl	$d_{obs.}(\text{Å})$	$d_{calc.}(\text{Å})$	$I_{obs.}$
003	5.13	5.13	m
101	2.527	2.527	tf
104	2.130	2.133	TF
107	1.677	1.669	tf
108	1.541	1.539	f
110	1.479	1.479	f
113	1.419	1.421	tf
0012	1.276	1.282	tf
1011	1.227	1.225	f

oxygen window. This diffusion requires a lot of energy and, accordingly, the cell polarization must be high.

The presence of highly-charged cations in the sodium plane leads to a strong contraction of the intersheet distance (i.e., of parameter c). The crystallographic formula of the charged phases can be written $(Na_xTi_y\square_{1-x-y})(Ti_{1-y}\square_y)O_2$ with $x < 0.67$. It should be noted that y increases continuously during the charge and it turns out that the material can no longer be considered as a layer compound, but rather as a tridimensional one.

During discharge from this phase, the two bidimensional Na_xTiO_2 phases (O'3 and O3) do not reappear. The Na^+ ions fill the two types of available sites and a composition close to $(Na_{1-y}Ti_y)(Ti_{1-y}Na_y)O_2$ is reached without modification of the framework. The parameters of the discharged phase depend on the value of y attained during the overcharge. In Figure 5, the variation of parameters with x is given for two different values of y.

During reintercalation, there is no driving force which would lead to the migration of the titanium ions to their original positions. As a result, the transition is irreversible.

Acknowledgements

References

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