

ELECTROCHEMICAL ASPECTS OF THE DEINTERCALATION OF LAYERED AMO_2 COMPOUNDS

S. KIKKAWA*, S. MIYAZAKI and M. KOIZUMI

The Institute of Scientific and Industrial Research, Osaka University, Osaka 567 (Japan)

Summary

The electrochemical deintercalation of AMO_2 compounds, where $A = Li$ or Na , and $M = Cr, Co$ or Fe , was investigated. The open circuit voltage of $A/1M \text{ AlClO}_4\text{-propylene carbonate}/A_xMO_2$ cells and the chemical diffusion constant, \bar{D} , of alkali in A_xMO_2 were measured using a current-pulse relaxation technique. The cells made from lithium compounds showed an OCV of about 4 V. The voltage increased continuously with charging. The cell OCV of sodium compounds increased discontinuously in the range 2.4 - 3.2 V. The discontinuity was related to the change of MO_2 layer stacking in the deintercalation process. The highest diffusivity of $\bar{D}(Na) = 5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ was observed in Na_xCoO_2 ($0.5 < x < 0.6$). Diffusion constants were larger for trigonal prismatically surrounded sodium than for that octahedrally coordinated. Lithium diffused faster than sodium in the compounds having the same kind of transition metal in an octahedral environment.

Introduction

Deintercalation corresponds to the charging process of a secondary battery. Electrochemical deintercalations of $LiCoO_2$ and $NaMO_2$, where $M = Cr, Co, Ni$ [1, 2], have been investigated. Open circuit voltages and chemical diffusion constants of Na have not yet been obtained for the series of $NaMO_2$ compounds. In the present investigation the electrochemical deintercalation of AMO_2 compounds having ordered rock-salt structures, where $A = Li, Na$, and $M = Cr, Co, Fe$, was attempted. The open circuit voltage (OCV) of $A/1M \text{ AlClO}_4\text{-propylene carbonate}/A_xMO_2$ cells, and the chemical diffusion constant, \bar{D} , of alkali in A_xMO_2 , were measured by a current-pulse relaxation technique of Basu and Worrell [3].

Experimental results and discussion

The open circuit voltage of $Li/1M \text{ LiClO}_4$ in propylene carbonate/ Li_xCoO_2 was 3.8 V at $x = 1.0$. It gradually increased to ca. 4 V with decreasing

*To whom correspondence should be addressed.

amounts of lithium, as observed by Mizushima *et al.* [1]. The product charged to 4.0 V had a chemical composition of $\text{Li}_{0.5}\text{CoO}_2$ and was isostructural with LiCoO_2 . Hexagonal lattice parameters were $a = 2.816 \text{ \AA}$, $c = 14.08 \text{ \AA}$ for LiCoO_2 and $a = 2.810 \text{ \AA}$, $c = 14.41 \text{ \AA}$ for $\text{Li}_{0.5}\text{CoO}_2$. The interlayered lithium is octahedrally surrounded by oxygens in this composition range. A continuous increase of OCV from 3.65 V to 3.95 V was similarly observed with an Li_xCrO_2 cell in the composition range $1.0 \geq x \geq 0.8$.

The OCV of an $\text{Na}/1\text{M NaClO}_4\text{-propylene carbonate}/\text{Na}_x\text{CoO}_2$ cell changed discontinuously as a function of sodium content as seen in Fig. 1, and ranges from 2.4 to 3.7 V. Such step-wise potential change agrees well with the results reported by Delmas *et al.* [4]. However the x compositions for every potential step are smaller in the present study than in the previous report, probably because the applied current density is lower in the present case. The chemical compositions of products charged to 3 V were determined, by atomic absorption, as $\text{Na}_{0.5}\text{CoO}_2$. The discontinuous potential change was related to the alteration of sodium coordination from octahedral to trigonal prismatic. Single phases of *O3* and of *P3* were observed, respectively, in the compositional range $0.8 \leq x \leq 1.0$ and $0.5 \leq x \leq 0.65$. Phase mixtures were in the range $0.65 \leq x \leq 0.8$. A discontinuous potential

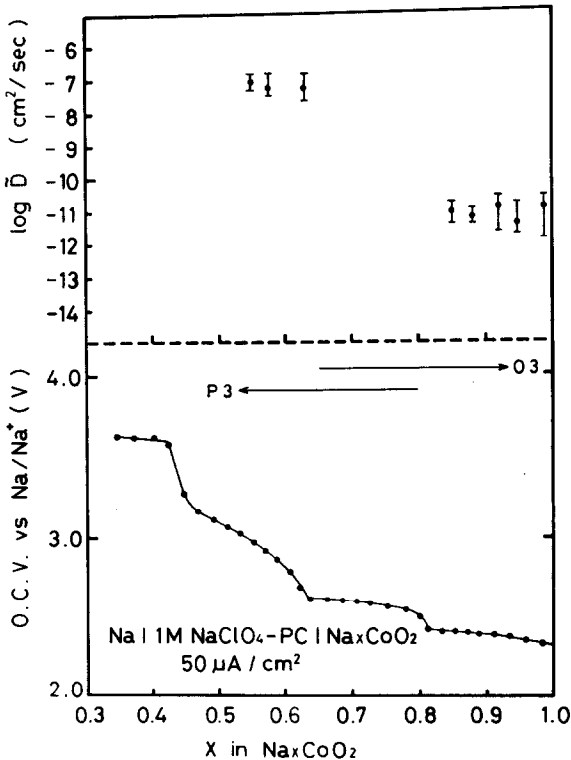


Fig. 1. Open circuit voltage of the $\text{Na}/1\text{M NaClO}_4$ in propylene carbonate/ Na_xCoO_2 cell and the chemical diffusivity of sodium in Na_xCoO_2 against the amount of sodium (x).

TABLE 1

Chemical diffusivity and OCV of A_xMO_2 at normal temperature

Compound	Composition	OCV (V)	\tilde{D} ($\text{cm}^2 \text{s}^{-1}$)	Type of coordination*
Na_xCoO_2	$0.9 < x < 1.0$	2.45 - 2.40	10^{-11}	O
	$0.5 < x < 0.6$	3.30 - 2.61	5×10^{-8}	T
Na_xCrO_2	$0.9 < x < 1.0$	2.67 - 2.60	10^{-12}	O
	$0.5 < x < 0.6$	3.24 - 3.03	10^{-10}	T
Na_xFeO_2	$0.9 < x < 1.0$	3.35 - 3.29	10^{-14}	O
Li_xCoO_2	$0.5 < x < 1.0$	4.20 - 3.80	5×10^{-9}	O
Li_xCrO_2	$0.8 < x < 1.0$	3.94 - 3.65	5×10^{-12}	O

*O: octahedral; T: trigonal prismatic.

change in the range 2.6 - 3.25 V in an Na_xCrO_2 cell ($1.0 \geq x \geq 0.5$) was similarly observed. In the case of Na_xFeO_2 , the OCV continuously increased from 3.29 V to 3.35 V in the composition range $1.0 \geq x \geq 0.9$. Further deintercalated products beyond $x = 0.9$ had a ferromagnetic impurity.

Chemical diffusion constants were measured using the current-pulse relaxation technique. The lithium diffusivity in Li_xCoO_2 was $5 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ independent of composition. This agrees well with the value determined by Mizushima *et al.* using the electrochemical galvanostatic intermittent titration method proposed by Weppner and Huggins [1, 5]. The lithium is always octahedrally coordinated by oxygen atoms in Li_xCoO_2 . The diffusion constant in Li_xCoO_2 is similar to that in Li_xTiS_2 , $10^{-9} - 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ [3, 6]. On the other hand, the sodium diffusivity in Na_xCoO_2 varied with composition as shown in Fig. 1. The average diffusivity value is $10^{-11} \text{ cm}^2 \text{ s}^{-1}$ in the composition range $0.8 \leq x \leq 1.0$. CoO_2 layers stack according to the O3 type and the interlayered Na^+ ions are octahedrally surrounded by oxygens. With a decrease in the amount of sodium, the interlayer distance expands and the CoO_2 layer packing type changes to P3. The average diffusivity value is $5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ in the range $0.5 < x < 0.63$. Only the P3 phase was observed, and the Na^+ ions are in trigonal prismatic sites in this compositional range. The sodium diffusivity is larger by two orders of magnitude in the P3 phase than in the O3 phase. Similar results could be observed on Na_xCrO_2 , as summarized in Table 1. $\tilde{D}(\text{Na}) = 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ in the O3 phase and $\tilde{D}(\text{Na}) = 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ in the P3 phase.

It is recognized from Table 1 that lithium diffuses faster than sodium in the O3 phase of compounds having the same kind of transition metal. $\tilde{D}(\text{Li}) = 5 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ and $\tilde{D}(\text{Na}) = 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ in cobalt compounds. $\tilde{D}(\text{Li}) = 5 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ and $\tilde{D}(\text{Na}) = 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ in chromium compounds. The reason for the difference cannot be specified, but the lithium ion is smaller in size and more electropositive than sodium.

References

- 1 K. Mizushima, P. C. Jones, P. J. Wiseman and J. B. Goodenough, *Mater. Res. Bull.*, 15 (1980) 783.
- 2 C. Delmas, J. J. Braconnier, A. Maazaz and P. Hagenmuller, *Rev. Chim. Miner.*, 19 (1982) 393.
- 3 S. Basu and W. L. Worrell, in P. Vashishta, J. N. Mundy and G. K. Shenoy (eds.), *Fast Ion Transport in Solids*, Elsevier-North-Holland, 1979, p. 149.
- 4 J. J. Braconnier, C. Delmas, C. Fouassier and P. Hagenmuller, *Mater. Res. Bull.*, 15 (1980) 1797.
- 5 W. Weppner and R. A. Huggins, *J. Electrochem. Soc.*, 124 (1977) 1569.
- 6 M. S. Whittingham, *Prog. Solid State Chem.*, 12 (1978) 41.