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Lithium-ion Insertion/Extraction Reaction with λ-MnO_2 in the Aqueous Phase

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The topotactic insertion of Li^+ in λ-MnO_2 involved an evolution of oxygen and a reduction of Mn(IV) to Mn(III) in a (LiCl + LiOH) solution. The major reaction could be represented as $\lambda\text{-}MnO_2 + xLiOH \longrightarrow Li_xMnO_2 + (x/2)H_2O + (x/4)O_2$, where x denotes moles of inserted Li^+ per mole of λ-MnO_2. The extraction of the inserted Li^+ was studied by using a solution containing either an acid(HCl) or an oxidizing agent(Br_2, $K_2S_2O_8$).

Recently, spinel-type manganese oxide(λ-MnO_2) has been prepared by extracting Li^+ from $LiMn_2O_4$ with acid¹⁾ or an oxidizing agent.²⁾ Hunter proposed a disproportionation mechanism for the topotactic extraction of Li^+ ($2LiMn_2O_4 + 4H^+ \longrightarrow 3\lambda\text{-}MnO_2 + 2Li^+ + Mn^{2+} + 2H_2O$).¹⁾ Xiang-mu and Clearfield proposed an ion-exchange mechanism ($LiMn_2O_4 + H^+ \longrightarrow HMn_2O_4 + Li^+$).³⁾ We have studied the insertion reactions of alkali metal ions with λ-MnO_2 in the aqueous phase.⁴⁾ The insertion reaction could scarcely proceed in a solution of each alkali metal chloride except Li^+ ions, the insertion of which took place effectively only in the presence of OH^- ions. We explained the selective insertion of Li^+ based on the "ion-sieve" effect of the tetrahedral vacant (or protonated) sites of the cubic closed-packed oxygen framework. The pH titration suggested a H^+/Li^+ ion-exchange mechanism for the Li^+ insertion. However, we have found the evolution of oxygen and the reduction of Mn(IV) to Mn(III) during the Li^+ insertion. In the present report, we will propose a redox mechanism for the major reaction of the topotactic insertion of Li^+ in alkaline solutions.

λ-MnO_2 was prepared by the acid treatment of $LiMn_2O_4$.⁴⁾ The lithium content of the product(λ-MnO_2) was 0.29 $mmol \cdot g^{-1}$, indicating that more than 92% of the lithium was extracted by the acid treatment. Metal ion insertion was carried out by mixing λ-MnO_2 with a (MCl + MOH, M= Li^+, K^+) solution at 25 °C. The concentrations of metal ions(Li^+, K^+, dissolved Mn) in the supernatant were determined by atomic absorption spectrometry and the OH^- concentration by titration with acid. The metal ion uptakes by λ-MnO_2 were calculated from the decreased metal ion concentrations and the amount of OH^- consumed from the decreased OH^- concentration. The evolution of gas was measured volumetrically in a helium gas atmosphere at 25 ± 0.5 °C. The gas composition was analyzed by gas chromatography with ZSM5 packing. Extraction of Li^+ was carried out by mixing the Li^+-inserted λ-MnO_2 with a solution containing 0.2-M HCl(1 M = 1 $mol \cdot dm^{-3}$), 0.1-M Br_2, or 0.2-M $K_2S_2O_8$ at 25 °C.

The MnO_2 substances were analyzed for available oxygen, as well as Mn, Li^+, K^+, Cl^-, and water contents. The available oxygen was determined by the standard oxalic acid method.[5)] After dissolving manganese oxide with a mixed solution of acid and H_2O_2, the Li^+, K^+, and Mn contents were determined by atomic absorption spectrometry and the Cl^- content by ion chromatography. The water content was calculated from the weight loss by heating at 400 °C in air. The chemical composition was calculated according to a method described in the literature.[6)] A powdered X-ray diffraction analysis was carried out.

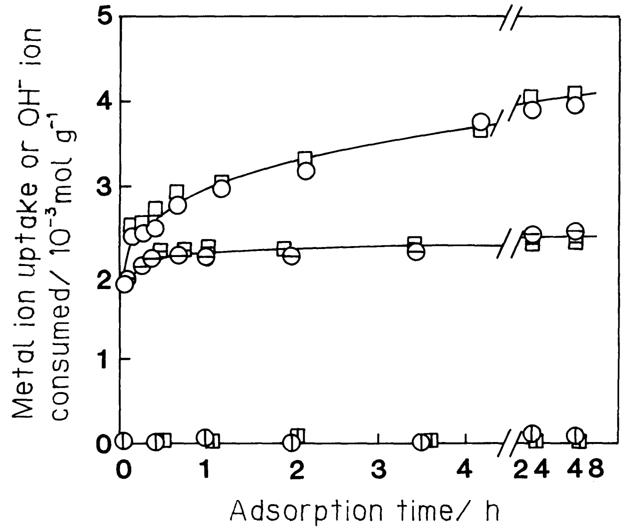

Fig. 1.
Time courses of metal ion insertion in λ-MnO_2 at 25 °C.
Circles and squares represent the amounts of metal ions inserted and OH^- consumed, respectively.
λ-MnO_2: 3.0 g,
volume of soln.: 300 cm^3.
○ □: (0.1-M LiCl + 0.050-M LiOH)
⊖ ⊟: (0.1-M LiCl + 0.025-M LiOH)
⦶ ◫: (0.1-M KCl + 0.025-M KOH)

The time dependences of Li^+ and K^+ insertions at 25 °C are illustrated in Fig. 1. In the case of a 0.025-M LiOH system, the insertion rate was relatively high; only 60 minutes was sufficient to reach 90% of the equilibrium uptake. In the case of a 0.050-M LiOH system, the insertion reaction was rapid up to a Li^+ uptake of 2.5 $mmol \cdot g^{-1}$, followed by a slow insertion phase. The amount of consumed OH^- was nearly equal to that of the inserted Li^+ over the insertion process. Supernatant solutions showed a slightly purplish color due to the presence of Mn(VII) ions. However, the concentration of Mn was less than 5×10^{-4} M. The equilibrium K^+-uptake was very small (less than 0.2 $mmol \cdot g^{-1}$) compared to the Li^+-uptake. The evolution of O_2 gas was observed in the case of Li^+ insertion (Fig. 2). The evolved amounts of the gas were found to be 0.57 and 0.84 mmol per gram of original λ-MnO_2 for 0.025-M LiOH and 0.050-M LiOH systems, respectively.

The X-ray diffraction analysis indicated that the crystal system of the metal ion-inserted sample was identical with that of λ-MnO_2. The lattice constant increased with the amount of inserted Li^+(Table 1). A chemical analysis showed that most of manganese in λ-MnO_2 is in a tetravalent state. The Mn:O ratio scarcely changed through the insertion of Li^+. This indicates a reduction of an equivalent amount of manganese from Mn(IV) to Mn(III) by Li^+ insertion. The Cl^- contents were less than 0.01 $mmol \cdot g^{-1}$ for all samples.

Table 1. Chemical Compositions and Lattice Constants

Sample	Chemical composition	Lattice constant(a_0)/nm[f]
λ-MnO_2	$Li_{0.03}MnO_{2.0}(H_2O)_{0.05}$	0.800
λ-MnO_2(Li-I)[a]	$Li_{0.25}MnO_{2.0}(H_2O)_{0.03}$	0.811
λ-MnO_2(Li-II)[b]	$Li_{0.39}MnO_{2.0}(H_2O)_{0.02}$	0.820
λ-MnO_2(K)[c]	$Li_{0.04}K_{0.005}MnO_{2.0}(H_2O)_{0.05}$	0.800
λ-MnO_2(Li-Br_2)[d]	$Li_{0.07}MnO_{2.0}(H_2O)_{0.05}$	0.802
λ-MnO_2(Li-HCl)[e]	$Li_{0.07}MnO_{2.0}(H_2O)_{0.04}$	0.802

a) λ-MnO_2 was treated with a (0.1-M LiCl + 0.025-M LiOH) solution for 1 d.

b) λ-MnO_2 was treated with a (0.1-M LiCl + 0.050-M LiOH) solution for 1 d.

c) λ-MnO_2 was treated with a (0.1-M KCl + 0.025-M KOH) solution for 1 d.

d) λ-MnO_2(Li-II) was treated with a 0.1-M Br_2 solution for 2 d.

e) λ-MnO_2(Li-II) was treated with a 0.2-M HCl solution for 2 d.

f) Lattice constant calculated from the X-ray diffraction pattern.

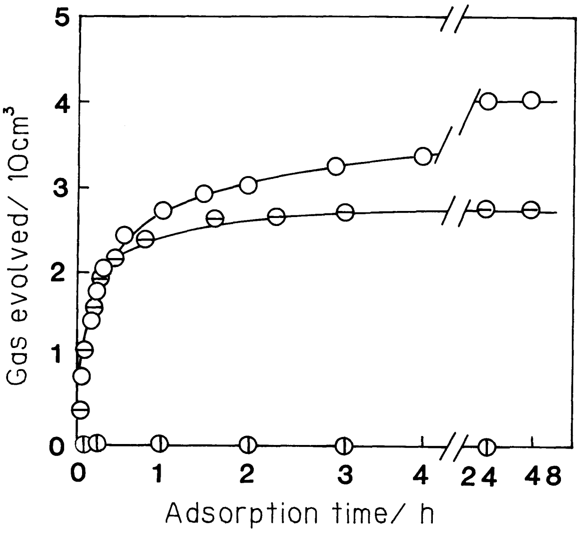

Fig. 2.
Time courses of gas evolution during the insertion of metal ions.
Suspension: 2 g λ-MnO_2 in 180 cm^3 H_2O
Volume of metal ion solution: 20 cm^3
○: (1-M LiCl + 0.50-M LiOH)
⊖: (1-M LiCl + 0.25-M LiOH)
⦶: (1-M KCl + 0.25-M KOH)

As a result of the above chemical analysis, the major reaction of the Li^+ insertion could be represented by the following chemical reaction using symbol x, moles of inserted Li^+ per mole of λ-MnO_2 ($0 < x < 0.5$):

$$MnO_2 + xLiOH \longrightarrow Li_xMnO_2 + (x/2)H_2O + (x/4)O_2. \qquad (1)$$

The amounts of evolved O_2 (0.57 and 0.84 mmol·g^{-1} for 0.025-M LiOH and 0.050-M LiOH systems, respectively) were about 85% of the expected values, 0.63 and 1.0 mmol·g^{-1}, respectively. The smaller amounts of the O_2 evolution are probably due to the presence of minor reaction of an ion-exchange adsorption. Equation 1 indicates that the Li^+ insertion consumes an equivalent amount of OH^- ions. This is the reason why the Li^+ insertion reaction could apparently be represented as the mechanism of an H^+/Li^+ ion exchange in the pH titration study in which only pH dependence of the Li^+ uptake by λ-MnO_2 was measured.[4] Equation 1 also shows that the Li^+ insertion in λ-MnO_2 proceeds through a unique reaction which involves the reduction of Mn(IV) and the oxidation of OH^- to O_2. This unique reaction can be well explained on the basis of the concept of the one-phase solid redox system proposed by Kozawa et al.⁷⁾ Manganese oxide has the characteristics that small ions(H^+, Li^+) and electrons(or positive charge) can move freely within the oxide structure to form a one-phase solid redox system. Therefore, the insertion reaction can be divided into two parts: 1)the insertion of Li^+ into a tetrahedral vacant site of the ccp oxygen framework of λ-MnO_2, accompaning a reduction of Mn(IV), and 2)the migration of excess positive-charge to the surface of λ-MnO_2 powder followed by the oxidization of OH^- in the aqueous phase.

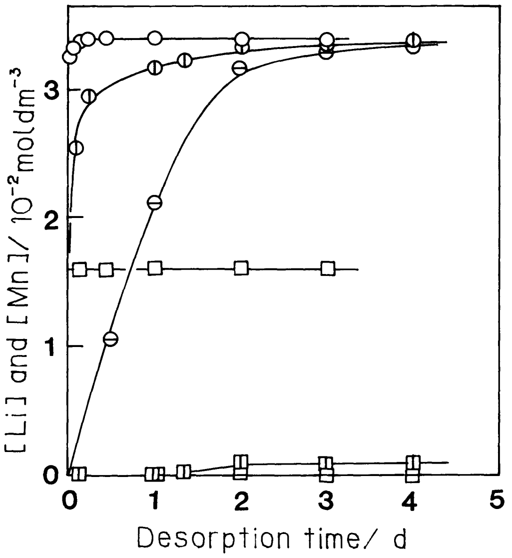

Fig. 3.
Time courses of Li^+ extraction at 25 °C. Circles and squares correspond to the concentrations of Li^+ and Mn, respectively.
Sample: λ-MnO_2(Li-II), 1 g, volume of soln.: 100 cm^3
○ □: 0.2-M HCl, ⦶ ◫: 0.1-M Br_2,
⊖ ⊟: 0.2-M $K_2S_2O_8$.

The rate of Li^+ extraction was rapid in a HCl solution: about 20 minutes was sufficient to reach equilibrium(Fig. 3). A dissolution of Mn was observed markedly in the HCl solution. The mole ratio of dissolved Mn to eluted Li^+ was 0.47, which is close to the expected ratio(0.5) in a Li^+-extraction reaction from $LiMn_2O_4$.¹⁾ In the case of oxidizing agents, the extraction of Li^+ could proceed with a slight dissolution of Mn. Samples after the extraction reaction maintained the same spinel structure as the original λ-MnO_2. A chemical analysis showed that most of the manganese was in a state of Mn(IV) after extraction (Table 1). These results suggest that the insertion/extraction of Li^+ proceeds reversibly in cooperation with a reduction/oxidation of manganese.

References

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