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ELECTROCHEMICAL RECOVERY OF LITHIUM IONS IN THE AQUEOUS PHASE

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ABSTRACT

The electrochemical insertion of lithium ions into a Pt/λ-MnO_2 electrode was investigated in various metal chloride solutions. The Li^+ insertion occurred effectively in LiCl solutions with higher concentration than 10 mmol/dm^3, but it could hardly occur in a 0.1 mmol/dm^3 LiCl solution. Alkaline earth metal ions showed a stronger inhibition effect against the Li^+ insertion into the Pt/λ-MnO_2 electrode than alkali metal ions. However, since only Li^+ ions were taken up from a mixed solution of lithium and alkaline earth metal chlorides, a high selectivity of the electrode for lithium ions was shown.

It was possible to recover lithium ions from geothermal water by this electrochemical method using the Pt/λ-MnO_2 electrode; the lithium uptake was 11 mg/g-MnO_2.

INTRODUCTION

Metallic lithium and various kinds of lithium compounds are highlighted in recent years as a material useful in a wide variety of applications including, for example, ceramic materials, dry batteries, absorption refrigerants, medicines and so on (1, 2). It is expected further that the future demand for metallic lithium and lithium compounds will expand to a large extent in the fields of large-capacity batteries, aluminum-based alloys, fuels in nuclear fusion-type reactors and others consequently with a rapid growth of the overall consumption of lithium materials throughout the world (1).

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In order to reply such a growth of demand for lithium, we have studied the recovery of lithium from sea water using a spinel-type manganese oxide (λ-MnO_2) as an adsorbent (3-5). We have also studied the adsorptive properties of λ-MnO_2 (6-10) and the mechanism for Li^+insertion to λ-MnO_2 in the aqueous phase (11). As a result, we have proposed the redox mechanism for Li^+ insertion into λ-MnO_2, accompanying a reduction of Mn(IV) to Mn(III) and an oxidation of OH^- to oxygen gas (9), and further confirmed that the electrochemical insertion of lithium ions into a Pt/λ-MnO_2 electrode selectively occurs in the aqueous phase according to the redox mechanism (12).

In the present study, we investigate the electrochemical insertion of Li^+ into the Pt/λ-MnO_2 electrode in various solutions and examine the feasibility to recover lithium from geothermal water.

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EXPERIMENTAL

Preparation of Electrode

A Pt/λ-MnO_2 electrode was produced by the electrochemical extraction of Li^+ from a Pt/$LiMn_2O_4$ electrode prepared by a thermal decomposition method as described previously (12). A small amount of a mixed solution of $LiNO_3$ and $Mn(NO_3)_2$ (2 mol/dm^3, Li/Mn mole ratio = 0.5) was brushed on a Pt plate (10 x 10 x 0.3 mm^3) forming a thin layer of the solution. After drying at room temperature, the plate was heated to 1093 K for a few minutes and then cooled to room temperature. This brushing-heating treatment was repeated 15 times. Finally, the plate was annealed at 1093 K for 5 min to form the Pt/$LiMn_2O_4$ electrode. X-ray diffraction analysis showed the formation of a uniform spinel phase of $LiMn_2O_4$ (ASTM No. 18-736) with a lattice constant of 0.825 nm. The Li/Mn ratio of the electrode was found to be 0.47.

The electrochemical extraction of $Li^+$was carried out by applying a constant potential (1 V vs. calomel electrode (2 mol/dm^3 KCl)) to the Pt/$LiMn_2O_4$ electrode in a 10 mmol/dm^3 LiCl solution at 298 K. After the electric current was decreased from 1.5 mA to less than 5 μA, the Pt plate was washed with water and air dried. The X-ray analysis of the Pt/λ-MnO_2 electrode showed a topotactic Li^+ extraction had occurred with a slight decrease of the lattice constant to 0.805 nm. Its Li/Mn ratio was found to be 0.01, indicating that more than 97% of Li^+ was extracted from the Pt/$LiMn_2O_4$ electrode.

X-ray and Atomic Absorption Analyses

An X-ray diffraction pattern was obtained on a Rigaku RINT 1200 diffractometer. Atomic absorption analysis was performed on a Shimadzu AA-670 atomic absorption spectrophotometer.

Cyclic Voltammetry

The insertion/extraction reactions of alkali or alkaline earth metal ions with the Pt/λ-MnO_2 electrode were investigated in 20 cm^3 of metal chloride solutions at 298 K by cyclic voltammetry on the following sweep condition: the forward sweep (potential decrease from 1 to 0.2 V) and the reverse sweep (potential increase from 0.2 to 1 V) at various scan rates. Calomel and Pt-wire electrodes were used as reference and counter electrodes, respectively.

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Lithium Uptake from Metal Chloride Solutions or Geothermal Water

The lithium uptake by the Pt/λ-MnO_2 electrode was evaluated after the forward sweep from 1 to 0.2 V at the scan rate of 0.1 mV/s in various solutions. The Mn and Li content of the electrode was determined by atomic absorption spectrometry after dissolving the oxide layer with a mixed solution of 1N HCl and H_2O_2.

Recovery of Lithium Ions from Geothermal Water

The main chemical constituents in the geothermal water were as follows: Li, 5.19 ppm; Na, 1,060 ppm; K, 151 ppm; Mg, 0.10 ppm; Ca, 16.4 ppm; Ba, 0.10 ppm; Si, 31 ppm; SO_4^-, 127 ppm; Cl, 1,890 ppm (13). After the Li^+ insertion into the Pt/λ-MnO_2 electrode in the geothermal water, the lithium ions were extracted into a 0.1 mmol/dm^3 LiCl solution from the Li^+-inserted electrode. This insertion/extraction process was repeated 5 times, and then the Li content of the electrolyte was determined.

RESULTS AND DISCUSSION

Effect of Scan Rate on Cyclic Voltammogram

Figure 1 shows cyclic voltammograms of the Pt/λ-MnO_2 electrode in a 10 mmol/dm^3 LiCl solution. Two distinct peaks were observed for both the forward

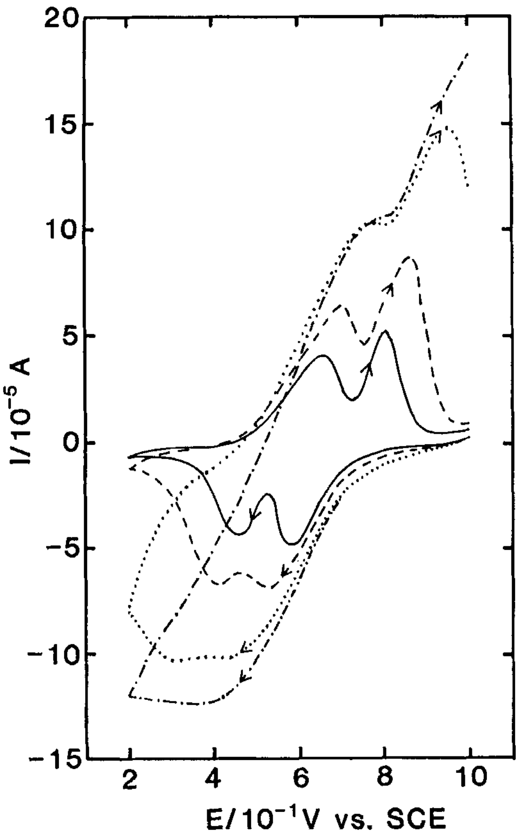

FIGURE 1. Effect of scan rate on cyclic voltammogram of the Pt/ λ-MnO$_2$ electrode in 20 cm^3 of a 10 mmol/dm^3 LiCl solution. Scan rate: 0.1 mV/s (——), 0.2 mV/s (- - -), 0.5 mV/s (· · ·), and 1 mV/s (- · · -).

and the reverse sweeps at a scan rate below 0.1 mV/s, probably caused by the presence of two types of sites in λ-MnO$_2$ with different insertion/extraction potentials for Li$^+$ (12). The cyclic voltammograms varied depending on the sweep condition. The increase in the scan rate caused an increase in the peak current, accompanying shifts of both the anodic and the cathodic current peaks in noble and less noble directions, respectively. The two distinct peaks changed to a single peak at a scan rate above 0.5 mV/s. These results suggest that the insertion of Li$^+$ is a

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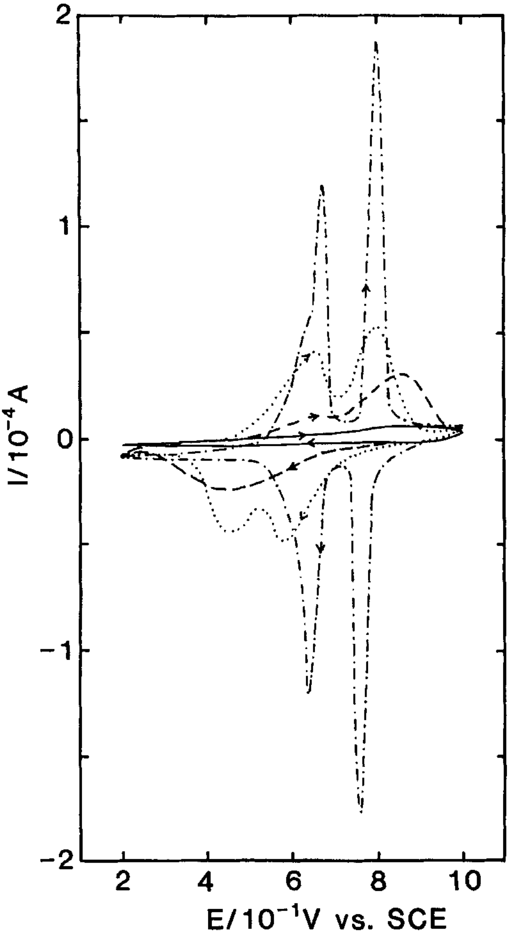

FIGURE 2. Effect of concentration of LiCl on cyclic voltammogram. Scan rate: 0.1 mV/s. Concentration of LiCl solution: 0.1 mmol/dm^3 (——), 1 mmol/dm^3 (- - -), 10 mmol/dm^3 (· · ·), and 0.1 mmol/dm^3 (- · · -).

TABLE 1. VALUES OF LATTICE CONSTANT (a_0) AND Li/Mn MOLE RATIO IN THE ELECTRODE AFTER FORWARD SWEEP[a]

Electrolyte	a_0/nm	Li/Mn
0.1 mmol/dm^3 LiCl	0.803	0.01
1 mmol/dm^3 LiCl	0.821	0.25
10 mmol/dm^3 LiCl	0.825	0.40
0.1 mol/dm^3 LiCl	0.824	0.45

[a] Forward sweep: 1 to 0.2 V (vs. SCE) at the scan rate of 0.1 mV/s.

TABLE 2. VALUES OF LATTICE CONSTANT (a_0) AND METAL/Mn MOLE RATIO IN THE Li^+-INSERTED ELECTRODE[a]

Electrolyte[b]	a_0/nm	Li/Mn	Mg/Mn	Ca/Mn	Sr/Mn	Ba/Mn
$LiCl+MgCl_2$	0.823	0.34	0.002	-	-	-
$LiCl+CaCl_2$	0.822	0.32	-	0.003	-	-
$LiCl+SrCl_2$	0.824	0.33	-	-	n.d.[c]	-
$LiCl+BaCl_2$	0.824	0.33	-	-	-	n.d.
$LiCl+MCl_2$	0.823	0.25	0.001	0.002	n.d.	n.d.
(M=Mg, Ca, Sr, and Ba)						

[a] Sweep condition: 1 to 0.2 V (vs. SCE) at the scan rate of 0.1 mV/s.
[b] Concentration of every metal chloride is 10mmol/dm^3.
[c] n.d. : Not detected (metal/Mn ratio is less than 0.001.)

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relatively slow process compared with the usual electrochemical reaction involving electron transfer. This may be mainly due to the low conductivity of Li^+ in the manganese oxide layer or in the laminar film.

Effect of Concentration of LiCl on Li^+ Insertion

The cyclic voltammogram also depended on the concentration of the LiCl solution as shown in Figure 2. The decrease of the concentration caused a decrease in the peak current, accompanying a shift of the cathodic current peak to a less noble direction. The two distinct peaks were observed in the solution with the

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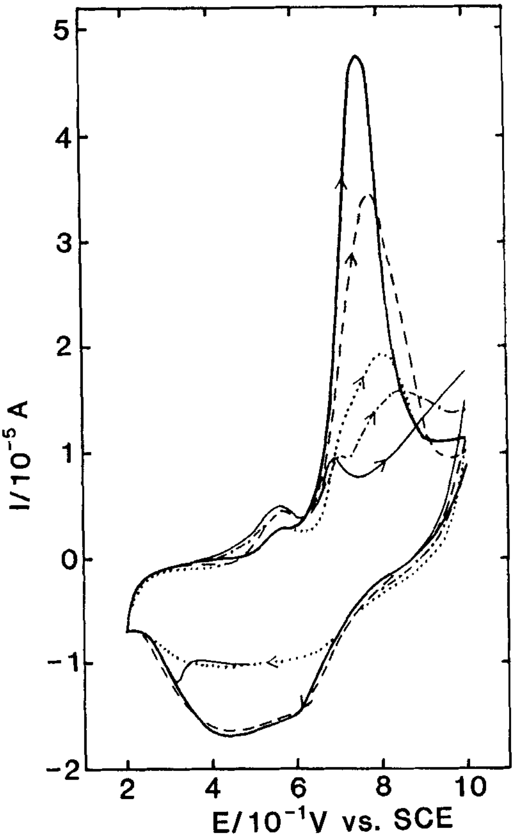

FIGURE 3. Cyclic voltammograms of multiple insertion/extraction cycles with geothermal water. Scan rate: 0.1 mV/s. Number of cycles: 1st scan (——), 2nd scan (- - -), 3rd scan (· · ·), 5th scan (- · · -), and 10th (——).

higher concentration than 10 mmol/dm^3 at the scan rate of 0.1 mV/s, but not in the case of the concentration below 1 mmol/dm^3. Besides, the cyclic voltammogram in a 0.1 mmol/dm^3 LiCl solution showed little electric current, suggesting that it is difficult to recover lithium ions from such a dilute solution on this sweep condition.

Actually, the result of the insertion experiment showed that the lattice constant and the Li/Mn ratio of the electrode after the forward sweep were 0.803 nm and 0.01, respectively, indicating that lithium ions can be hardly inserted into the Pt/λ-MnO_2 electrode in the 0.1 mmol/dm^3 LiCl solution (Table 1). On the other hand, lithium ions were effectively taken up from the LiCl solutions with the higher concentration than 10 mmol/dm^3.

Effect of Metal Ions on Li^+ insertion

The cyclic voltammogram in a mixed solution of LiCl + alkaline earth metal chlorides was almost the same as that in the LiCl solution and little influence of these divalent metal ions was observed. However, Table 2 shows that these divalent ions inhibited the Li^+ insertion into the Pt/λ-MnO_2 electrode and decreased the lithium uptake. Although small amounts of Mg^{2+} and Ca^{2+} ions were detected on the electrode, a high selectivity of the Pt/λ-MnO_2 electrode for Li^+ was observed. The inhibition effect by alkaline earth metal ions was stronger than that by alkali metal ions, which have the slight effect (12). The alkaline earth metal ions may be adsorbed on the electrode surface by electrostatic interaction (14) or surface complex formation (15) and this may cause the decrease of the lithium uptake. Since both the electrostatic interaction and the complexation ability of alkaline earth metal ions are stronger than those of alkali metal ions, the former are likely to have the stronger effect than the latter.

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Recovery of Lithium Ions from Geothermal Water

Figure 3 shows the cyclic voltammograms of 10 insertion/extraction cycles in the geothermal water at the scan rate of 0.1 mV/s. The cyclic voltammogram for the first scan is similar to that in the 1 mmol/dm^3 LiCl solution (Figure 2), because the geothermal water contains 0.75 mmol/dm^3 (5.2 ppm) of Li^+ and other ions in the solution probably had only a slight effect during the first scan. The repetition of the cycle changed the pattern of the voltammogram, especially in the anodic side. In the experiments of the multiple cycles in the various mixed solutions, alkali metal or alkaline earth metal ions did not change the voltammogram. However, since the voltammograms of the multiple cycles in the mixed solution of Li^+ and silicate ions gave the similar pattern to that in the geothermal water, silicate ions probably interfere with the Li^+ insertion/extraction by the adsorption on the surface of the Pt/λ-MnO_2 electrode.

The Li/Mn ratio of the electrode after the Li^+ insertion in the geothermal water was found to be 0.13, corresponding to 11 mg/g-MnO_2. And the total amount of Li^+ of 3 μmol was obtained in the recovery experiment, in which the Li^+ insertion into the Pt/λ-MnO_2 electrode in the geothermal water and the Li^+ extraction from the Li^+-inserted electrode to the dilute solution of LiCl were repeated 5 times.

In conclusion, lithium ions can be effectively recovered from aqueous solutions by the electrochemical method using the Pt/λ-MnO_2 electrode.

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