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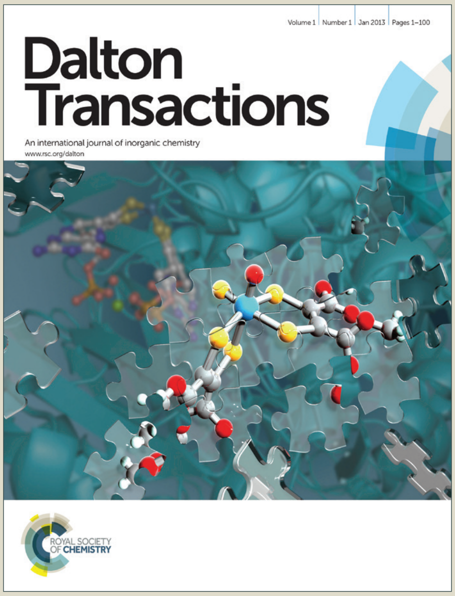

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ARTICLE

# Lithium recovery from salt lake brine by $H_2TiO_3$

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The details of ion exchange properties of layered $H_2TiO_3$, derived from layered $Li_2TiO_3$ precursor upon treatment with HCl solution, with lithium ions in the salt lake brine (collected from Salar de Uyuni, Bolivia) are reported. The lithium adsorption rate is slow, requiring 1 d to attain an equilibrium at room temperature. The adsorption of lithium ions by $H_2TiO_3$ follows the Langmuir model with adsorptive capacity of 32.6 mg/g (4.7 mmol/g) at pH 6.5 from the brine containing $NaHCO_3$ ($NaHCO_3$ added to control pH). The total amount of sodium, potassium, magnesium and calcium adsorbed from the brine was < 0.30 mmol/g. The $H_2TiO_3$ is found capable to efficiently adsorb lithium ions from the brine containing competitive cations such as sodium, potassium, magnesium and calcium in extremely large excess. The results indicate that the selectivity order $Li^+ >> Na^+, K^+, Mg^{2+}, Ca^{2+}$ originates from a size effect. The $H_2TiO_3$ can be regenerated and reused for lithium exchange in the brine with exchange capacity very similar to the original $H_2TiO_3$.

## Introduction

Lithium and its compounds have several commercial applications, including heat-resistant glass and ceramics, lithium-ion battery for electric devices and electric vehicles, pharmaceuticals etc.[1] Lithium can be obtained from different sources, such as igneous rocks (spodumene and petalite), brine lake deposits (also referred as Salar), and seawater.[1,2] Brines with high lithium concentrations (ca. 0.3%) are located in Salar of Bolivia, Chile and Argentina.[1,2] Although the ocean contains lithium with estimated amount of $2 \times 10^6$ Mt, essentially making it an unlimited source, but production of lithium from seawater is still 10–30 times more costly than production from spodumene and brines, because of low lithium concentration in seawater (0.17 mg/dm$^3$).[2]

Lithium from the brine is obtained as lithium carbonate by the evaporation process, which consists of evaporating salty water for 12–18 months in ponds using solar energy.[2] Brine contains a mixture of salts, such as chlorides and sulfates of sodium, potassium, magnesium, calcium, boron and lithium that are recovered by evaporation in the ponds. The most interfering element is magnesium, because lithium has similar ionic properties as magnesium, with ionic radius nearly identical (0.07 nm) thus making it difficult to separate lithium from magnesium.[2]

Different methods for lithium recovery from the brine or artificial brine have been reported. An et al.[3] reported the hydrometallurgical process, using two-stage precipitation for lithium recovery from the salt lake brine, collected from Salar de Uyuni, Bolivia. Unlike other commercial Salar brines currently being processed, the high levels of magnesium and sulfate in Uyuni brine would create difficulties during processing, if the conventional techniques are used.[3] Recently, electrochemical method based on the rechargeable battery principle for lithium recovery from salt water comprising 5 mol dm$^{-3}$ NaCl and 0.2–50 mmol dm$^{-3}$ LiCl or salt water comprising equal concentrations of LiCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$ (30 mmol dm$^{-3}$) has been reported[4,5] This method has not been reported for lithium recovery from the real brine solutions. Other method that can remove lithium ions from the solution is ion-exchange. Typically, ion-sieve manganese oxides derived from $LiMn_2O_4$, $Li_{1.5}Mn_2O_4$, $Li_{1.33}Mn_{1.67}O_4$ and $Li_{1.6}Mn_{1.6}O_4$ upon treatment with acid have been proven extremely efficient for lithium recovery from the seawater.[6–11] In the previous works,[12,13] we described ion-sieve materials such as $H_{1.33}Mn_{1.67}O_4$, $H_{1.6}Mn_{1.6}O_4$ and magnesium doped manganese oxides, which can undergo ion-exchange reaction in the brine. These spinel compounds were shown to be highly effective in lithium recovery from the salt brine.[12,13]

In an attempt to find other ion-exchange materials based on titanium oxides for lithium recovery from the brine, $H_2TiO_3$ derived from $Li_2TiO_3$ precursor upon treatment with acid was selected. The $Li_2TiO_3$ can be described in three structural modifications, α, β, and γ:[14] the metastable cubic *α*-phase (space group *Fm*-3*m*), which transforms at above 300°C to monoclinic β-phase (space group *C*2/*c*) is stable up to 1155°C, after which it transforms to cubic γ- $Li_2TiO_3$. $Li_2TiO_3$ is a technologically important material with applications such as an electrode material in lithium-ion batteries[15,16] and solid breeder material in the blanket of DT fusion reactor.[17]

It has been reported that the percent of lithium extracted in $Li_2TiO_3$ with acid solutions depends on the preparation conditions; the low temperature phase of monoclinic $Li_2TiO_3$ synthesized at 700°C shows nearly complete lithium extraction (100%) with acid to form monoclinic $H_2TiO_3$, whereas the high temperature phase synthesized at 1000°C shows partial lithium extraction (ca. 50%).[18] The difference in chemical reactivity between the low temperature and high temperature monoclinic $Li_2TiO_3$ phases is due to the presence of defects, mainly stacking faults in the structure.[18] The structural, spectroscopic and adsorption properties of $H_2TiO_3$ have been examined.[18–22] From a series of adsorptions of alkali metal ions using 0.10 mol $dm^{-3}$ solutions (MCl + MOH, M = Li, Na, K, Rb and Cs) with $H_2TiO_3$, it was concluded that the material had a strong preference for only lithium ion and in general, the reaction proceeded in the presence of added base, reflecting a weak cation exchanger.[19]

Since the demand of lithium has been increasing drastically in recent years, there are concerns on the supply of lithium. The economic feasibility of lithium extraction depends on both its lithium concentrations and the process used to extract lithium from lithium sources. Lithium can be extracted from hard rock or salt brine via months of evaporation, then processed to lithium carbonate. Both methods of lithium production are time consuming.[1] To date, there has been little research focused on lithium extraction from the salt brine by ion exchange method, which is the underlying motivation for this study. The goal of this study is to demonstrate the ion-exchange method using $H_2TiO_3$, which describes the lithium extraction from the salt brine by laboratory-scale experiments. We demonstrated that $H_2TiO_3$ exhibits extremely high selectivity toward lithium ions in the salt brine, and the lithium adsorption is not influenced by various coexisting cations such as sodium, potassium, calcium and magnesium ions.

There has been, to our knowledge, no study of lithium ion-exchange reaction of the $H_2TiO_3$ in the brine. Here, we report lithium recovery from the salt brine by $H_2TiO_3$, which exhibited lithium adsorptive capacity comparable to those of ion-sieve manganese oxides $H_{1.33}Mn_{1.67}O_4$ and $H_{1.6}Mn_{1.6}O_4$.

## Experimental

### Synthesis of $Li_2TiO_3$ and $H_2TiO_3$

The $Li_2TiO_3$ was synthesized as described with modification of calcination time and acid-treatment time.[18,19] Anatase type $TiO_2$ (15.0 g, Ti 0.187 mole) and $Li_2CO_3$ (13.9 g, 0.376 mole Li) were mixed, ground and heated in an alumina crucible at a rate of ca. 6°C $min^{-1}$ in air up to 700°C and maintained at 700°C for next 4 h. After cooling to room temperature, the solid powder ($Li_2TiO_3$) was treated with 0.2 mol $dm^{-3}$ HCl solution with occasional shaking for 1 d at room temperature (1 g of solid in 1 $dm^3$ acid). The solid was separated by filtration, washed with deionized water until the filtrate was neutral and left to dry at room temperature to obtain the $H_2TiO_3$.

### Characterization

Powder X-ray diffraction (XRD) of the materials were obtained by an X-ray diffractometer (RINT 2100; Rigaku Corp.) operated at 40 kV and 24 mA with Cu K$\alpha$ radiation at a scanning rate of 1° ($2\theta$) $min^{-1}$. Lattice constant parameters for the materials were determined using a JADE 3.0 package. Thermogravimetric-differential thermo analysis (TG-DTA) was carried out by thermal analyzer (Rigaku Thermo plus TG 8110). 10 mg (±0.02) of $H_2TiO_3$ and 10 mg (±0.02) $\alpha$-$Al_2O_3$ as a reference material were heated on platinum crucibles up to 800°C at a heating rate of 10°C $min^{-1}$ in air. SEM images were obtained using a field emission scanning electron microscope (JSM-6700FZ; JEOL). FT-IR measurement was carried out using a Perkin Elmer type Spectrum 100 spectrometer with an ATR accessory (Specac, Standard Golden Gate).

For chemical analysis of Ti and Li, 50 mg of the material was placed in a beaker containing 10 $cm^3$ of 9 mol $dm^{-3}$ $H_2SO_4$, and the beaker was covered with watch glass. The material was dissolved by acid digestion at ca. 80°C. The contents of Ti and Li in the solutions after appropriate dilutions were determined by ICP atomic emission spectrometer (SPS 7800; Seiko Instruments, Inc.), and atomic absorption spectrometry (AAnalyst 300; Perkin Elmer), respectively.

### Salt Lake Brine

Raw brine was collected from Salar de Uyuni, Bolivia. The pH of the raw brine was 6.7. The brine was analyzed for Li, Na, K. Mg and Ca by atomic absorption spectrometry and Cl, $NO_3$ and $SO_4$ by ion chromatography (761 Compact IC, Metrohm AG); Li = 1630, Na = 59000, K = 18700, Mg = 29000, Ca = 230, Cl = 240000, $SO_4$ = 26000 and $NO_3$ = 970 (mg $dm^{-3}$).

### Lithium extraction in $Li_2TiO_3$

In order to select the appropriate concentration of acid to extract lithium ions in $Li_2TiO_3$, $Li_2TiO_3$ (0.20 g) was reacted with 20 $cm^3$ HCl of 0.10, 0.20, 0.30 or 0.50 mol $dm^{-3}$, and stirred for 1 d at room temperature. The suspensions were filtered using 0.45 μm syringe-driven filter unit. The filtrates were analyzed for Li and Ti contents.

The rate of lithium extraction in $Li_2TiO_3$ was carried out by stirring 2.5 g of $Li_2TiO_3$ in 250 $cm^3$ HCl solution (0.2 mol $dm^{-3}$) at room temperature, and aliquots (2 $cm^3$) were collected at different intervals of time to analyze lithium contents.

### Kinetic study of lithium adsorption from the $NaHCO_3$-added brine

In order to evaluate the lithium adsorption rate at pH ca. 6.5, solid $NaHCO_3$ was added to the raw brine (25 g $NaHCO_3$ in 1.0 $dm^3$ brine). $H_2TiO_3$ (1.0 g) was treated with 50 $cm^3$ of the brine containing $NaHCO_3$ and the suspension was stirred at room temperature. Aliquots (0.50 $cm^3$) were sampled at different intervals of time. After centrifugation, the clear solutions were diluted for analysis of Li contents.

### Lithium adsorption isotherm from the $NaHCO_3$-added brine

The lithium adsorption data were determined at constant pH value of ca. 6.5 by dispersing 0.10–0.50 g of $H_2TiO_3$ in 10 $cm^3$ $NaHCO_3$-added brine and the suspensions were frequently shaken for 1 d. After centrifugation of the suspensions, the clear solutions were analyzed for Li contents.

### Lithium adsorption from the NaOH-added brine

The lithium adsorption from the brine, prepared at different 1 mol $dm^{-3}$ NaOH/brine (volume ratio) was investigated by dispersing 0.20 g of $H_2TiO_3$ in 10 $cm^3$ brine, and the suspension was frequently shaken for 1 d at room temperature.

The effect of sample dose (g $dm^{-3}$) on adsorptions of lithium, sodium, potassium, magnesium and calcium from the brine containing 1 mol $dm^{-3}$ NaOH (volume ratio of NaOH /

brine = 0.12) was carried out by dispersing 0.10–0.50 g of $H_2TiO_3$ in 10 $cm^3$ of the brine.

### Regeneration

For regeneration of $H_2TiO_3$, 1.0 g of lithium adsorbed sample (32 mg $g^{-1}$) was treated with 100 $cm^3$ of 0.2 mol $dm^{-3}$ HCl solution for 1 d at room temperature. Lithium was extracted completely (ca. 100%). To test the reusability of the regenerated sample, ca. 1.0 g of the acid treated material was treated with 50 $cm^3$ brine containing $NaHCO_3$ for 1 d.

## Results and discussion

### Characterization of the materials

The formulas of the as-synthesized lithium titanium oxide at 700°C and its protonated product were estimated from chemical analysis of the solid phases as $Li_{2.01}Ti_{0.99}O_3$ or $Li_2TiO_3$ (Li 12.4 wt%, Ti 42.3 wt%), and $H_{1.97}Ti_{1.02}O_3$ or $H_2TiO_3$ (Ti 50.2 wt%, $H_2O$ 18.2 wt%), respectively. The water content of $H_2TiO_3$ was estimated from the loss of mass at 500°C in the TG-DTA curves as described.[19]

The XRD pattern of the $Li_2TiO_3$ precursor is shown in Fig. 1a. The reflections of $Li_2TiO_3$ are sharp and the pattern can be indexed to monoclinic lattice; space group *C*2/*c* (JCPDS card 33-0831), $a$ = 5.13 Å, $b$ = 8.83 Å, $c$ = 9.78 Å, and β = 99.94°, which were in good agreement with the reported values ($a$ = 5.04 Å, $b$ = 8.80 Å, $c$ = 9.72 Å, β = 100.01°).[23] The crystal structure of $Li_2TiO_3$, better described by the formula $Li[Li_{1/3}Ti_{2/3}]O_2$ in relation with its layered structure, is shown in Fig. 2a.[23,24] The structure can be represented as a cubic close packing of oxygen atoms, with metal atoms placed in octahedral voids. Li and Ti form two types of layers in $Li_2TiO_3$ structure; one (Li) layer occupies only by Li atoms, whereas another ($LiTi_2$) layer occupies 1/3 of Li and 2/3 of Ti. Furthermore, lithium ions in the (Li) layer constitute 75% of the total number of lithium in the $Li_2TiO_3$ structure, whereas the remaining 25% are located in the ($LiTi_2$) layers.[25]

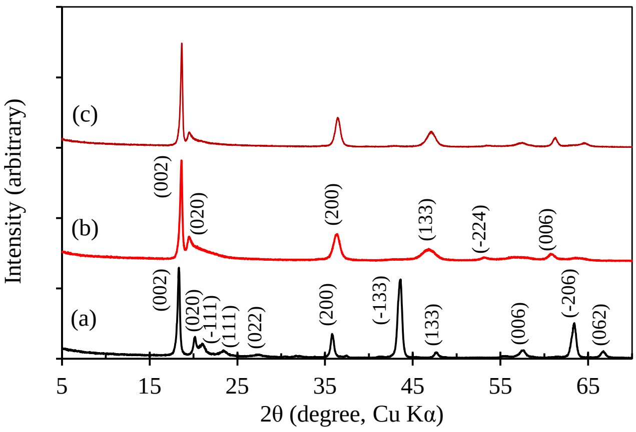


Fig. 1. a) XRD patterns of $Li_2TiO_3$; b) $H_2TiO_3$; c) $H_2TiO_3$ upon lithium exchange.

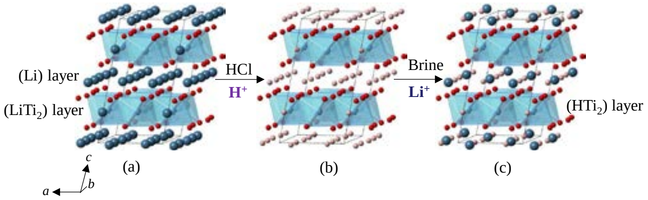
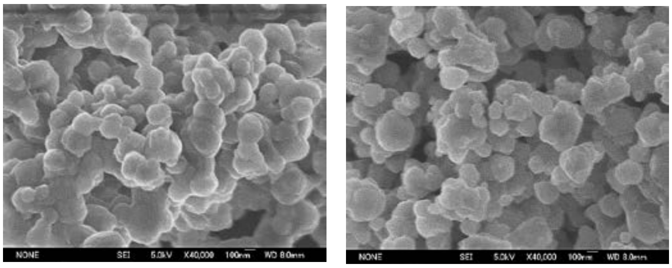


Fig. 2. a) Crystal structure of layered $Li_2TiO_3$; b) $H_2TiO_3$; c) $H_2TiO_3$ upon lithium exchange. ($TiO_6$ as octahedra, Li as blue ball, H as light pink ball)

The XRD pattern of the $H_2TiO_3$ was similar to that of the $Li_2TiO_3$ precursor as shown in Fig. 1b. A decrease in the intensity of the reflections from the $H_2TiO_3$ was observed at $2\theta$ value > 20° in the XRD pattern, and the reflections shifted slightly to a higher $2\theta$ value. The lattice parameters $a$ = 4.97 Å, $b$ = 9.08 Å, $c$ = 9.53 Å, and $\beta$ = 99.86° were in good agreement with the reported values for $H_2TiO_3$ ($a$ = 4.96 Å, $b$ = 8.89 Å, $c$ = 9.48 Å, β = 100.1°).[20] The $H_2TiO_3$ adopts layered monoclinic structure (space group *C*2/*c*), similar to that of the $Li_2TiO_3$ precursor (Fig. 2b).[20,26] The SEM image of $Li_2TiO_3$ showed that the plate-like particles were agglomerated and the average diameter of the particles was in the range of 100-200 nm (Fig. 3a). The particle shape of $H_2TiO_3$ with less agglomeration was similar to $Li_2TiO_3$ precursor (Fig. 3b). This indicated that lithium extraction in $Li_2TiO_3$ progressed topotactically, preserving the layered structure.



(a) (b)

Fig. 3. SEM images. a) $Li_2TiO_3$; b) $H_2TiO_3$.

### Lithium extraction in $Li_2TiO_3$

Lithium extractions in $Li_2TiO_3$ were performed using different concentrations of HCl solutions (Fig. 4a). The amount of lithium extracted was only 50 % (64.7 mg $g^{-1}$ or 9.4 mmol $g^{-1}$) with 0.10 mol $dm^{-3}$ HCl solution due to availability of less amount of protons (9.6 mmol $g^{-1}$) in the solution; this indicates that lithium extraction proceeded by consuming nearly an equivalent amount of protons in the solution. The amount of lithium extracted increased to 99–100% with 0.20, 0.3 and 0.5 mol $dm^{-3}$ HCl solutions. During contact of the $H_2TiO_3$ with 0.10 or 0.2 mol $dm^{-3}$ HCl solution, the dissolution of Ti from the solid into the solution was not detected from the analysis of the supernatant solution. However, the dissolution of Ti appeared in the HCl solutions above 0.20 mol $dm^{-3}$.

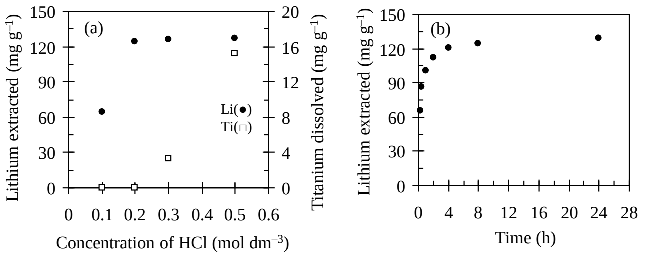


Fig. 4. a) Lithium extraction and dissolution of titanium upon treatment of $Li_2TiO_3$ with HCl solutions; b) Rate of lithium extraction from $Li_2TiO_3$ with 0.2 mol dm$^{-3}$ HCl.

The kinetic of lithium extraction in $Li_2TiO_3$ was conducted with 0.2 mol dm$^{-3}$ HCl solution (Fig. 4b). The percent of lithium extracted was nearly 100% at proton/lithium molar ratio of 1.0; the rate was found to be slow requiring 1 d for complete lithium extraction. Very slow lithium extractability rates in monoclinic $Li_2TiO_3$ precursors were reported by other researchers; nearly complete lithium extraction (ca. 100%) occurred from $Li_2TiO_3$ in 0.5 mol dm$^{-3}$ $HNO_3$ by changing acid every day for 14 d at room temperature [19] or in 0.1 mol dm$^{-3}$ HCl at 60°C for 3 d.[22] It can be expected that very slow lithium extractability rate in $Li_2TiO_3$ occurred from longer calcination time of the $Li_2TiO_3$ precursors (calcination at 700°C, 24 h)[19,22] compared to the present $Li_2TiO_3$ (calcination at 700°C, 4h). A complete lithium extraction (ca. 100%) was achieved within 4 h in $Li_2TiO_3$ (calcination at 700°C, 5h) with 0.05 mol dm$^{-3}$ acetic acid at 60°C.[18]

Fig. 5 shows the FTIR spectra of $H_2TiO_3$ with peaks at 3488, 3040, 1926 and 1625 cm$^{-1}$. The peak at 3488 cm$^{-1}$ is OH stretching vibration of hydroxyl groups related to $H^+/Li^+$ exchange, and the peaks at 3040 and 1625 cm$^{-1}$ are stretching and bending vibrations of the OH groups of adsorbed water. The peak at 1926 cm$^{-1}$ could not be identified. Raman spectra of $H_2TiO_3$ showed also one broad band at 3000 cm$^{-1}$ due to hydrogen-bonded OH groups and one narrow band at 3500 cm$^{-1}$ due to isolated O-H bonds uninvolved in the interaction with other oxygen-hydrogen groups.[18]

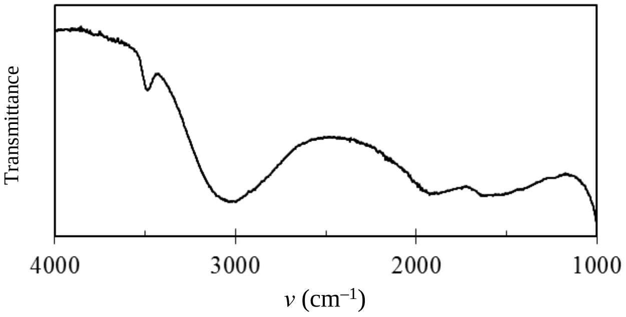


Fig. 5. FT-IR of $H_2TiO_3$.

From the studies of $^7$Li NMR(MS) spectra of partially protonated samples of $Li_2TiO_3$, it was concluded that lithium ions in the (Li) layers were first exchanged to form $H[Li_{1/3}Ti_{2/3}]O_2$, followed by further exchange of lithium ions in the ($LiTi_2$) layers to form fully exchanged phase $H[H_{1/3}Ti_{2/3}]O_2$.[18]

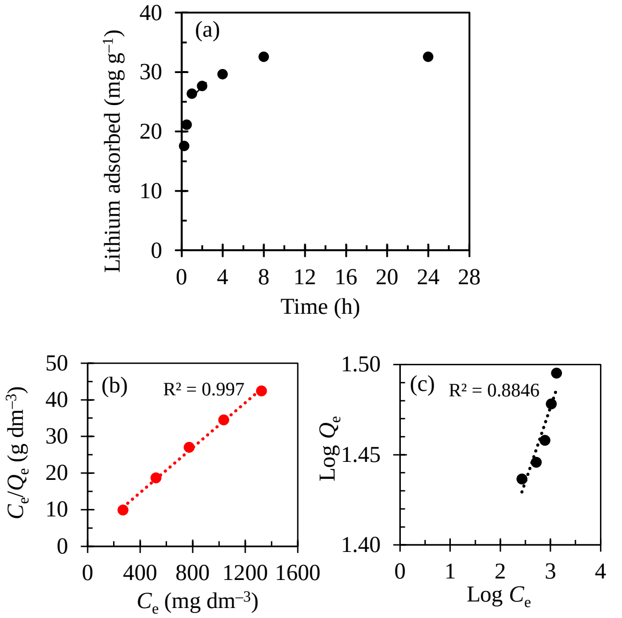


Fig. 6. a) Lithium adsorption rate from the $NaHCO_3$-added brine by $H_2TiO_3$; b) Langmuir adsorption isotherm; c) Freundlich adsorption isotherm.

## Kinetics of lithium adsorption from the brine

If the raw brine is used for lithium adsorption, the pH of the brine decreases due to the release of protons from the adsorbent. Since $NaHCO_3$ acts as a buffer in the brine, the pH of the brine before and after lithium adsorption was nearly the same (ca. 6.5). Lithium adsorption experiments were performed from the $NaHCO_3$-added brine by a batch method at pH ca. 6.5. The rate of lithium adsorption is shown in Fig. 6a. Remarkably, $H_2TiO_3$ is able to adsorb the lithium ions with initial adsorption of 26 mg g$^{-1}$ within 1 h followed by slow lithium adsorption requiring 24 h to attain equilibrium. The lithium adsorptive capacity was found to be 32.0 mg g$^{-1}$, similar to ion-sieve manganese oxides requiring 8 h to attain an equilibrium with capacity of 32.0 mg g$^{-1}$.[12] An extremely high concentration of Na, K, Mg and Ca in salt brine did not affect the lithium selectivity, showing the $H_2TiO_3$ with lithium ion-sieve property.

## Lithium adsorption isotherm

To assess the lithium adsorptive capacity of $H_2TiO_3$ from the $NaHCO_3$-added brine, the isotherm for lithium adsorption was determined at pH 6.5. The experimental data are presented in Fig. 6b and Fig. 6c for the Langmuir (eq. 1) and Freundlich (eq. 2) isotherm models, respectively, expressed as

$$q = q_m\,[bC_e/(1+bC_e)] \qquad (1)$$

$$q = K_F C_e^{1/n} \qquad (2)$$

where $q$ denotes the amount of lithium adsorbed (mg g$^{-1}$) by the $H_2TiO_3$ at the equilibrium concentration $C_e$ (mg dm$^{-3}$), $q_m$ signifies the maximum adsorptive capacity (mg g$^{-1}$), and $b$ (dm$^3$ mg$^{-1}$) represents the Langmuir constant related to the free energy of the material, and $K_F$ and $n$ respectively denote Freundlich constants related to the lithium adsorptive capacity and the lithium interaction of the material. The best fitting of the isotherm data was achieved with the Langmuir model ($q_m$ = 32.6 mg g$^{-1}$, $b$ = 0.013 dm$^3$ mg$^{-1}$, $R^2$ = 0.997) compared to that of Freundlich model ($K_F$ = 17.0, $n$ = 12.1, $R^2$ = 0.885). The Langmuir model[27] assumes that the maximum adsorption corresponds to a saturated monolayer of cations, all the exchange sites are equivalent and the energy of adsorption is constant over all sites, and the adsorption occurs at definite, and localized sites. In contrast, the Freundlich model[27] assumes that adsorption occurs on a heterogeneous surface, where adsorption sites exhibit a spectrum different binding energies. The maximum lithium adsorptive capacity $q_m$ of the $H_2TiO_3$ was found to be 32.6 mg $g^{-1}$. This capacity compares well with ion-sieves $H_{1.33}Mn_{1.67}O_4$ and $H_{1.6}Mn_{1.6}O_4$ showing capacity of 32.0 mg $g^{-1}$.[12] The XRD pattern of the $H_2TiO_3$ upon lithium exchange is shown in Fig. 1c ($a$ = 4.99 Å, $b$ = 9.13 Å, $c$ = 9.64 Å, and $\beta$ = 99.87°). The inserted protons in the interlayer space of $H_2TiO_3$ are re-exchanged for lithium ions (Fig. 2c).

The maximum lithium adsorptive capacity was found to be 32.6 mg $g^{-1}$ (4.7 mmol $g^{-1}$), which is only 26% of theoretical capacity for lithium (126 mg $g^{-1}$ or 18.1 mmol $g^{-1}$). This theoretical capacity of the $H_2TiO_3$ is based on the assumption that only lithium ions are exchanged to form $Li_2TiO_3$. From the lithium adsorption studies in 0.1 mol/$dm^3$ LiOH or LiCl solutions, the $H_2TiO_3$ exhibited lithium capacities of 4.0–5.8 mmol $g^{-1}$.[19,21,22] Ariza et al.[8] reported that the existence of all inserted protons in $H_{1.33}Mn_{1.67}O_4$ and $H_{1.6}Mn_{1.6}O_4$ spinels cannot be re-exchanged completely for lithium from LiOH solution. It can be assumed that the existence of inserted protons in the ($HTi_2$) layers of $H_2TiO_3$ cannot be re-exchanged for lithium ions from the brine, thereby exhibiting low lithium adsorptive capacity of the $H_2TiO_3$. In a different study of $Li_2TiO_3$ treated with molten $AgNO_3$ at 300°C, it is confirmed that silver ions cannot be exchanged with lithium ions at the ($LiTi_2$) layers, but can be exchanged at (Li) layers forming a layered material $Ag[Li_{1/3}Ti_{2/3}]O_2$.[28]

## Lithium adsorption from the NaOH-added brine

The NaOH solution was added to the raw brine to study lithium adsorption at different pH values. Effects of NaOH addition into the brine for lithium adsorption by $H_2TiO_3$ are shown in Fig. 7a. The lithium adsorptive capacity from the raw brine was remarkably low (15.8 mg $g^{-1}$) in the absence of NaOH, because the brine pH decreased from 6.7 to 4.3 due to release of protons from the solid into the solution. As expected, the addition of NaOH solution into the brine caused a gradual increase in lithium adsorptive capacity due to increase in final pH of the brine. The maximum capacity was found to be 31.5 mg $g^{-1}$ at NaOH / brine volume ratio of 0.12 and sample dose of 20 g $dm^{-3}$. Lithium adsorption reaction caused pH decrease as seen from the difference between the initial and final pH values.

Further experiments on adsorptions of lithium, sodium, potassium, magnesium and calcium were performed at different sample doses (g $dm^{-3}$) in the brine containing 1 mol $dm^{-3}$ NaOH (volume ratio of NaOH/brine = 0.12). The amounts of cations adsorbed by $H_2TiO_3$ were determined after dissolving the solid in $H_2SO_4$ solution. The results (Fig. 7b) showed that lithium adsorption decreased markedly with increase in sample dose due to decrease in corresponding final pH values i.e. release of protons from the solid into the solution. The maximum lithium adsorptive capacity was found to be 32.7 mg $g^{-1}$ (4.7 mmol $g^{-1}$) at sample dose of 10 g $dm^{-3}$, whereas the total adsorption of sodium, potassium and magnesium was very low (<0.3 mmol $g^{-1}$), and the presence of calcium ions in the test solutions was not detected. The high lithium adsorptive capacity of $H_2TiO_3$ can be explained by the lithium ion-sieve property of the material. The exchange sites are so narrow that Na (0.102 nm), K (0.138 nm) and Ca (0.100 nm) with ionic radii larger than Li (0.074 nm) cannot enter the exchange sites in the interlayer space due to steric effect. Although ionic radius of Mg (0.072 nm) is close to Li (0.074 nm), a high energy is required for the dehydration of magnesium ions to enter the exchange sites because the free energy of hydration for Mg ($\Delta G_h^0$ = –1980 kJ $mol^{-1}$) is four times the Li ($\Delta G_h^0$ = –475 kJ $mol^{-1}$).[29]

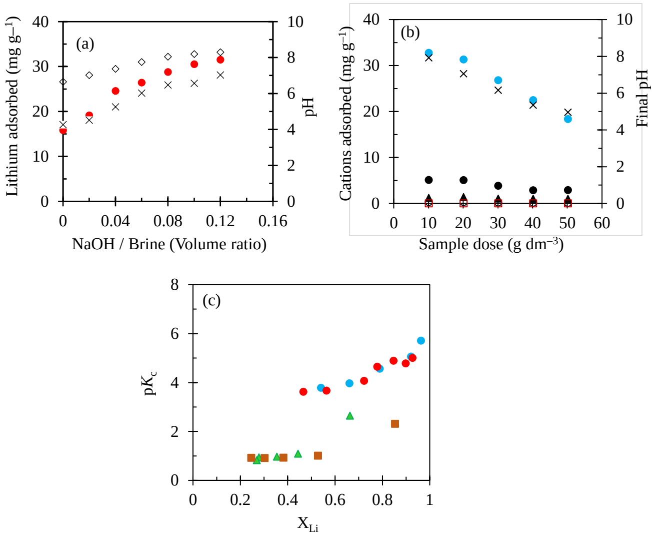


Fig. 7. a) Lithium adsorption from the NaOH-added brine by $H_2TiO_3$: Li(●), initial pH(◊), final pH(×); b) Effect of sample dose on adsorption of cations by $H_2TiO_3$: Li(●), Na(●), K(▲), Mg(○), Ca(□), final pH(×); c) p$K_c$ vs. $X_{Li}$ calculated from Fig. 7a (●), Fig. 7b (●), $H_{1.33}Mn_{1.67}O_4$ (▲) from ref. 12 and $H_{1.6}Mn_{1.6}O_4$ (■) from ref. 12.

## Regeneration

By reacting lithium adsorbed sample (32.0 mg $g^{-1}$ from the $NaHCO_3$-added brine) with 0.20 mol $dm^{-3}$ HCl solution, the exchange of the lithium ions by protons can be achieved. The regenerated material showed the lithium adsorptive capacity of 31.4 mg $g^{-1}$ (ca. 98%) of the original $H_2TiO_3$.

## Lithium adsorption mechanism

From the above results, the lithium adsorption from the brine by $H_2TiO_3$ caused a decrease in brine pH due to release of protons from the solid into the solution accompanying $Li^+/H^+$ exchange. The $Li^+/H^+$ exchange caused no change in the crystal structure of the material. The results of lithium adsorption from the brine can be discussed on the basis of ion-exchange reaction as follows;[30]

$$H^+_{(s)} + Li_{(l)} \rightarrow Li^+_{(s)} + H^+_{(l)} \qquad (3)$$

where $H^+_{(s)}$, $Li_{(s)}$ refer to species in the solid phase, and $Li_{(l)}$, $H^+_{(l)}$ refer to species in the solution phase. The equilibrium constant, $K$, of equation (3) can be written as

$$K = \{(H^+_{(l)})X_{Li}/(Li_{(l)})X_H\}(f_{Li}/f_H) \qquad (4)$$

where $X_{Li}$ and $X_H$ are the mole fractions of the lithium ions and protons in the solid phase, $f_{Li}$ and $f_H$ are activity coefficients of lithium and proton in the solid phase, and ( $H^+_{(l)}$) and ($Li_{(l)}$) are activities of protons and lithium ions in the solution phase, respectively. The selectivity coefficient ($K_c$) can be calculated from the lithium adsorption data as follows;[30]

$$pK_c = pH - \log(X_{Li}/X_H) + \log[Li] \qquad (5)$$

where [Li] is the concentration of lithium ions in the solution phase. The p$K_c$ values calculated from the Fig. 7a and 7b are plotted as a function of $X_{Li}$ in Fig. 7c. The p$K_c$ values of $H_{1.33}Mn_{1.67}O_4$ and $H_{1.6}Mn_{1.6}O_4$ are also plotted using the lithium adsorption data from the brine.[12] In the region $X_{Li}$ < 0.6 for

$H_2TiO_3$, the p$K_c$ values were nearly constant (ca. 3.8). The intrinsic selectivity coefficient p$K_c^0$ value (the p$K_c$ value extrapolated to $X_{Li} = 0$) was found to be ca. 3.8, larger than those of $H_{1.33}Mn_{1.67}O_4$ and $H_{1.6}Mn_{1.6}O_4$ (p$K_c^0 = 1$). In the region $X_{Li} > 0.6$, the p$K_c$ value increased with increase in $X_{Li}$, probably due to the steric effect. The p$K_c$ values of $H_2TiO_3$ are larger than those of $H_{1.33}Mn_{1.67}O_4$ and $H_{1.6}Mn_{1.6}O_4$ over the whole range of $X_{Li}$, indicating that $H_2TiO_3$ has exchange sites with lower acidity than those of other two. This indicates that $H_2TiO_3$ exhibits lithium ion exchange reaction in the brine, showing an extremely high concentrations of cations in salt brine did not affect the lithium selectivity.

## Conclusions

It was demonstrated that the layered $H_2TiO_3$ showed a remarkably high exchange capacity and selectivity for lithium ions in the real salt lake brine. The material exhibited maximum lithium exchange capacity of 32.7 mg $g^{-1}$ (4.7 mmol $g^{-1}$) from NaOH-added brine at sample dose of 10 g $dm^{-3}$, whereas the total capacity of sodium, potassium, magnesium and calcium was <0.3 mmol $g^{-1}$. The lithium adsorption reaction proceeds through ion-exchange reaction at the interlayer space of $H_2TiO_3$, similar to silver ion-exchange on the interlayer of $Li_2TiO_3$. This lithium adsorptive capacity of the $H_2TiO_3$ compares well with excellent ion-sieve materials $H_{1.33}Mn_{1.67}O_4$ and $H_{1.6}Mn_{1.6}O_4$ although the $H_2TiO_3$ has exchange sites with lower acidity than the other two. To the best our knowledge, the $H_2TiO_3$ represents the only example among the hydrated titanium oxides ever reported showing exceptional selectivity for lithium ions in the brine.

## Notes and references

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1 L. T. Peiro, G. V. Mendez and R. U. Ayres, *JOM*, 2013, **65**, 986-996.

2 H. Vikstrom, S. Davidsson and M. Hook, *Appl. Energy*, 2013, **110**, 252-266.

3 J. W. An, D. J. Kang, K. T. Tran, M. J. Kim, T. Lim and T. Tran, *Hydrometallurgy*, 2012, **117-118**, 64-70.

4 M. Pasta, A. Battistel and F. La Mantia, *Energy Environ. Sci*., 2012, **5**, 9487-9491.

5 J. Lee, S. H. Yu, C. Kim, Y. E. Sung and J. Yoon, *Phys. Chem. Chem. Phys*., 2013, **15**, 7690-7695.

6 K. Ooi, Y. Miyai, S. Katoh, H. Maeda and M. Abe, *Langmuir*, 1990, **6**, 289-291.

7 R. Chitrakar, H. Kanoh, Y. Miyai and K. Ooi, *Ind. Eng. Chem. Res.*, 2001, **40**, 2054-2058.

8 M. J. Ariza, D. J. Jones, J. Roziere, R. Chitrakar and K Ooi, *Chem. Mater*., 2006, **18**, 1885-1890.

9 R. Chitrakar, H. Kanoh, Y. Miyai and K. Ooi, *Chem. Mater.*, 2000, **12**, 3151-3157.

10 S. Nishihama, K. Onishi and K. Yoshizuka, *Solvent Extr. Ion Exch*., 2011, **29**, 421-431.

11 R. Chitrakar, H. Kanoh, Y. Makita, Y. Miyai and K. Ooi, *J. Mater. Chem*., 2000, **10**, 2325-2329.

12 R. Chitrakar, Y. Makita, K. Ooi and A. Sonoda, *Chem. Lett*., 2012, **41**, 1647-1649.

13 R. Chitrakar, Y. Makita, K. Ooi and A. Sonoda, *Bull. Chem. Soc. Jpn*., 2013, **86**, 850-855.

14 A. Laumann, K. T. Fehr, M. Wachsmann, M. Holzapfel and B. B. Iversen, *Solid State Ionics*, 2010, **181**, 1525-1529.

15 L. Zhang, X. Wang, H. Noguchi, M. Yoshio, K. Takada and T. Sasaki, *Electrochim. Acta*, 2004, **49**, 3305-3311.

16 L. H. Yang, C. Dong and J. Guo, *J. Power Sources*, 2008, **175**, 575-580.

17 G. Vitins, G. Kizane, A. Lusis and J. Tiliks, *J. Solid State Electrochem*., 2002, **6**, 311-319.

18 T. A. Denisova, L. G. Maksimova, E. V. Polyakov, N. A. Zhuravlev, S. A. Kovyazina, O. N. Leonidova, D. F. Khabibulin and E. I. You'eva, *Russ. J. Inorg. Chem*., 2006, **51**, 691-699.

19 S. Awano, A. Saiki, Y. Tamura and M. Abe, *J. Ion Exch*., 2003, **14**, 181-184.

20 Y. V. Baklanova, L. G. Maksimova, N. A. Zhuravlev, V. Y. Kavun and T. A. Denisova, *Bull. Russ. Aca. Sci.: Phys*., 2010, **74**, 1097-1099.

21 X. C. Shi, Z. B. Zhang, D. F. Zhou, L. F. Zhang, B. Z. Chen and L. L. Yu, *Trans. Nonferrous Met. Soc. China*, 2013, **23**, 253-259.

22 Q. H. Zhang, S. P. Li, S. Y. Sun, X. S. Yin and J. G. Yu, *Chem. Eng. Sci*., 2010, **65**, 165-168.

23 J. F. Dorrian and R. E. Newnham, *Mater. Res. Bull*., 1969, **4**, 179-184.

24 K. Kataoka, Y. Takahashi, N. Kijima, H. Nagai, J. Akimoto, Y. Idemoto and K. Ohshima, *Mater. Res. Bull*., 2009, **44**, 168-172.

25 M. Vijaykumar, S. Kerisit, Z. Yang, G. L. Graff, J. Liu, J. A. Sears, S. D. Burton, K. M. Rosso and J. Hu, *J. Phys. Chem. C*, 2009, **113**, 20108-20116.

26 A. N. Enyashin, T. A. Denisova and A. L. Ivanovskii, *Chem. Phys. Lett*., 2009, **484**, 44-47.

27 R. Han, W. Zou, Y. Wang and L. Zu, *J. Environ. Radioact*., 2007, **93**, 127-143.

28 Y. Hosogi, H. Kato and A. Kudo, *J. Mater. Chem*., 2008, **18**, 647-653.

29 Y. Marcus, *J. Chem. Soc. Faraday Trans*., 1991, **87**, 2995-2999.

30 K. Ooi, Y. Miyai, S. Katoh, H. Maeda and M. Abe, *Bull. Chem. Soc. Jpn*., 1988, **61**, 407-411.

## Graphical Abstract

Title: Lithium recovery from salt lake brine by $H_2TiO_3$

Authors: Ramesh Chitrakar, Yoji Makita, Kenta Ooi and Akinari Sonoda*

Texture abstract:

High lithium uptake of $H_2TiO_3$ from brine is due to lithium ion-sieve property. Exchange sites are narrow for Na, K, Mg, Ca to enter interlayer space due to steric effect.