



## Original Article

## Hydrogen isotope exchange behavior of protonated lithium metal compounds



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## ABSTRACT

The exchange behaviors of hydrogen isotopes between protonated lithium metal compounds and deuterated water or tritiated water were investigated. The various protonated lithium metal compounds were prepared by acid treatment of lithium metal compounds with different crystal structures and metal compositions. The protonated lithium metal compounds could more effectively reduce the deuterium concentration in water compared with the corresponding pristine lithium metal compounds. The  $H^+$  in the protonated lithium metal compounds was speculated to be more readily exchangeable with hydrons in the aqueous solution compared with  $Li^+$  in the pristine lithium metal compounds, and the exchanged heavier isotopes were speculated to be more stably retained in the crystal structure compared with the light protons. When the tritiated water (157.7 kBq/kg) was reacted with the protonated lithium metal compounds, the protonated lithium manganese nickel cobalt oxide was found to adsorb and retain twice as much tritium (163.9 Bq/g) as the protonated lithium manganese oxide (69.9 Bq/g) and the protonated lithium cobalt oxide (75.1 Bq/g) in the equilibrium state.

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## 1. Introduction

Tritium is a radioactive hydrogen isotope that decays into  $^3He$  by emitting low-energy beta particles ( $E_{max} = 18.6$  keV) [1,2]. Although tritium can be produced naturally in the upper atmosphere by cosmic rays, a substantial amount of tritium is also produced by nuclear facilities such as nuclear power plants and fuel reprocessing plants, which generate tritium-contaminated aqueous wastes [1]. In the case of heavy-water reactors, neutron bombardment of deuterium contained in heavy water mainly produces tritiated heavy water [1,3]. However, most of the tritium in the effluent stream of pressurized-water reactors originates from activation of boron dissolved in light water [1,3]. Tritium is mostly present as water isotopologues (HTO or DTO), and tritiated hydrogen gas (HT or DT) is also eventually oxidized into water in the environment [2,3]. Tritiated water behaves like normal water in the environment, and the unintended release of highly

concentrated tritiated water can result in contamination of surface water and groundwater. Tritiated water easily migrates because of the high mobility of water in the environment, and tritium can be partitioned in natural organisms and organic substances in the environment as a result of H/T chemical exchange reactions between tritiated water and the substances [2,3]. Consequently, hazardous internal exposure of the human body to radioactive tritium can occur through various pathways, including ingestion or skin absorption of tritiated water and inhalation of tritiated water vapor [2–4].

To reduce the environmental and health risks arising from radioactive tritium, researchers have developed technologies for separating tritium from contaminated water. The relatively large mass differences among hydrogen isotopes enables the efficient separation of tritium through water distillation [5], cryogenic gas distillation [6], water electrolysis [7,8], or catalytic chemical exchange [9]. Processes that combine several of these technologies [10], such as catalytic chemical exchange in conjunction with cryogenic distillation, have also been demonstrated, and commercial tritium removal facilities (TRFs) are being operated in Canada (Darlington TRF) [11] and South Korea (Wolsong TRF) [9,12].

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Nevertheless, such processes are energy and cost intensive; thus, more energy-efficient tritium separation technologies, such as adsorption [13–15] and membrane [16–19] technologies, are attracting increasing interest after the nuclear accident in Fukushima, Japan, that resulted in the generation of a tremendous amount of tritiated water (1,126,500 m<sup>3</sup> as of March 2019) [20,21]. However, separations of hydrogen isotopes by such technologies are still technically challenging and a comprehensive understanding of the underlying behavior of hydrogen isotopes is required for scientific and technical progresses in tritium separations.

Koyanaka et al. have reported that spinel-structured H<sub>x</sub>Mn<sub>2</sub>O<sub>4</sub> can efficiently remove tritium from light water by H<sup>+</sup>/T<sup>+</sup> exchange between tritiated water and the protons of H<sub>x</sub>Mn<sub>2</sub>O<sub>4</sub>; the authors speculated that slower transport of exchanged T<sup>+</sup> within the crystal influenced the tritium removal [13]. Moreover, the oxidation reaction of hydroxide ions (OT<sup>-</sup> → T<sup>+</sup> + 0.5O<sub>2</sub> + 2e<sup>-</sup>) caused by the metal oxide was assumed to generate more T<sup>+</sup> ions and enhance the removal of tritium from water. After tritium was removed by the metal oxide at the beginning of the reaction, however, the tritium concentration recovered to the initial concentration over time [13]. Although the protonated manganese oxide has shown promising performance for tritium separation, analysis of the hydrogen isotope exchange behaviors of various protonated lithium metal compounds has received little attention.

In the present paper, the exchange behaviors of hydrogen isotopes between various protonated lithium metal compounds and deuterated or tritiated water were investigated. The various protonated lithium metal compounds were prepared by acid treatment of lithium metal compounds having different crystal structures and metal compositions, including spinel-structured lithium manganese oxide (LMO), spinel-structured (LMNCO), layered lithium cobalt oxide (LCO), and olivine-structured lithium iron phosphate (LIP). A reduction of the deuterium or tritium concentration in water was observed after reactions of an aqueous solution with the various protonated lithium metal compounds, and the effects of the crystal structures and chemical components of the protonated lithium metal compounds on hydrogen isotope exchange was investigated.

## 2. Materials

LMO (LiMn<sub>2</sub>O<sub>4</sub>) was purchased from MSE Supplies (USA). LMNCO (Li<sub>1-x</sub>(Mn,Ni,Co)<sub>2+x</sub>O<sub>4</sub>), LCO (LiCo<sub>2</sub>O<sub>4</sub>), and LIP (LiFePO<sub>4</sub>) were obtained from CRM Materials (China) and were used without purification. Tritiated water (37 MBq/kg, Eckert & Ziegler Analytics) and deuterium oxide (99.9%, Sigma-Aldrich) were used after dilution with deionized water.

### 2.1. Preparation of protonated lithium metal compounds

Lithium metal compound powder (0.5 g) was mixed with 0.5 M HCl solution (1 L) in a polypropylene bottle, and the exchange reaction between Li<sup>+</sup> and H<sup>+</sup> was carried out for 1 h at 25 °C using a shaking incubator [13,22]. After the reaction, the particles were recovered by vacuum filtration using a polyvinylidene fluoride (PVDF) membrane filter (pore size = 0.45 μm), washed with deionized water, and air-dried.

For analysis of the metal components in protonated lithium metal compounds, the dried particles (100 mg) were digested with aqua regia solution (20 mL) for 10 h at 95 °C and the metal components in the solution were quantified by atomic absorption spectrometry (AAS, ContrAA 700, Analytik Jena, Germany).

### 2.2. Analysis of deuterium reduction in water by protonated lithium metal compounds

Deuterated water (10 wt%) was prepared by mixing D<sub>2</sub>O (100 g) and H<sub>2</sub>O (Milli-Q water, 900 g). The deuterated water was considered to contain 9.986 mmol/g of deuterium in water except for the naturally occurring deuterium contained in the deionized water. Each protonated lithium metal compound (300 mg) powder was dispersed in the 10 wt% deuterated water (15 g) and stirred for 24 h at 25 °C. The suspension was centrifuged, and the supernatant was filtered using an Amicon Ultra centrifugal filter (Millipore, molecular weight cut-off = 3 kDa).

The deuterium concentration in the supernatant (30 μL) was analyzed by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FT-IR, Nicolet iS5, Thermo Scientific). To obtain the deuterium concentration calibration curve, deuterated water samples with different concentrations (8 wt%–11 wt%) were prepared using D<sub>2</sub>O (99.9%) and ultrapure deionized water. The area of the HDO scissoring peak at 1450 cm<sup>-1</sup> was measured at each deuterium concentration (peak integration range: 1465–1400 cm<sup>-1</sup>, baseline: 1535–1340 cm<sup>-1</sup>), and the background peak area of deionized water was subtracted from the peak area obtained from the supernatant [23]. The deuterium concentration and reduced amount of deuterium in the supernatant were predicted using the calibration curve.

### 2.3. Analysis of tritium reduction in light water by protonated lithium metal compounds

Tritiated water (157.7 kBq/kg, 10 g) was prepared by dilution of a tritium stock solution (37 MBq/kg) with deionized water. The tritiated water was mixed with each protonated lithium metal compound (200 mg or 3 g) in a polypropylene tube and stirred for the desired time (10–80 min or 24 h) at 25 °C. The suspension was centrifuged, and the supernatant was filtered using an Amicon Ultra centrifugal filter (Millipore, molecular weight cut-off = 10 kDa).

The activity concentration of tritium in the supernatant was measured with a liquid scintillation counter (Hidex 300SL) for 10 h after the filtered solution (8 g) was mixed with a liquid scintillation cocktail (AquaLight, 12 g). The minimum detectable activity (MDA) of tritium was 0.007 kBq/kg under this measurement condition.

### 2.4. Distribution coefficient analysis

The distribution coefficient ( $K_d$ ) of deuterium or tritium was calculated using the equation

$$K_d = \frac{Q}{A} = \left( \frac{C_0}{C} - 1 \right) \frac{V}{M}$$

where  $Q$  and  $A$  are the equilibrium concentration of deuterium or tritium on the protonated lithium metal compound (mol/g or Bq/g) and in the aqueous solution (mol/g or Bq/g), respectively,  $C_0$  and  $C$  are the concentration of deuterium or tritium in the aqueous phase at the initial and equilibrium states, respectively, and  $V$  and  $M$  are volume of the solution (g) and the mass of the protonated lithium metal compound (g), respectively [24].

## 3. Results and discussion

### 3.1. Preparation of protonated lithium metal compounds

Protonated lithium metal compounds were prepared by simple acid treatment of the lithium metal compounds LMO, LMNCO, LCO, and LIP [13]. The corresponding lithium metal compounds are

denoted as PMO (protonated lithium manganese oxide), LMNCO (protonated lithium manganese nickel cobalt oxide), PCO (protonated lithium cobalt oxide), and PIP (protonated lithium iron phosphate), respectively.

To identify the pristine lithium metal compounds, the transition metal (Mn, Co, Ni) and Li contents in the lithium metal compounds were analyzed by AAS after acidic digestion of the samples in aqua regia (Table 1), and molar ratios of Li: transition metals were calculated (Table 2). The calculated molar ratios of Li: transition metal (Mn, Fe, or Co) for LMO, LCO, and LIP were 1 : 1.83, 1 : 0.95, and 1 : 1.07, respectively, and these ratios are similar to that of the ideal chemical compositions of  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiCoO}_2$  and  $\text{LiFePO}_4$ . Nevertheless, the Li and metal contents in the compounds were found to be slightly higher than expected, indicating presence of oxygen vacancies. The crystal structures of the pristine lithium metal compounds were analyzed by XRD, and the LMO, LCO, and LIP displayed typical XRD patterns of  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiCoO}_2$  and  $\text{LiFePO}_4$  (Fig. 1).

In the case of LMNCO, the Li: transition metal (Mn, Ni, Co) ratio was 1 : 2.56 and the Mn: Ni: Co molar ratio was 1 : 1.09: 0.97 (Table 2). Furthermore, LMNCO showed a typical XRD pattern of Li-deficient spinel-structured lithium metal compounds such as  $\text{Li}_{2-x}\text{NiMn}_{2-x}\text{O}_4$  [25], which agrees well with the results of the composition analysis. When the XRD and AAS analysis results were fully taken into account, the chemical formula of LMNCO was determined to be  $\text{Li}_{0.80}\text{Mn}_{0.67}\text{Ni}_{0.73}\text{Co}_{0.65}\text{O}_{4-x}$  with a spinel crystal structure and the vacant Li positions were assumed to be occupied by other residual transient metals such as Ni.

To verify the replacement of  $\text{Li}^+$  with  $\text{H}^+$  by acid-treatment, the transition metal (Mn, Co, Ni) and Li contents in the protonated lithium metal compounds were analyzed by AAS (Table 1). The Li contents in the compounds were lower after the acid treatment because  $\text{Li}^+$  was replaced by  $\text{H}^+$  via the treatment. The Li content was found to be reduced by 1.5 wt% after acid treatment of LMNCO, whereas the mole ratios of the transition-metal components were approximately the same (Table 1). In the case of PMO and PCO, the Li contents were reduced by 4.1 wt% and 0.5 wt%, respectively, compared with the Li contents in pristine LMO and LCO. However, the acid treatment of LIP resulted in reductions of the Li and Fe contents by 4.2 wt% and 15.6 wt%, respectively, compared with their initial weight fractions, indicating that Fe was dissolved from the compound during the acid treatment.

The changes in crystal structures of the compounds after the acid treatment were characterized by XRD analysis. With the exception of LIP, the compounds did not show substantial changes in their crystal structures after the acid treatment, although slight peak shifts to higher diffraction angles were observed. These observations are consistent with the results of previous reports of slight shrinkage of crystal structures of lithium metal compounds as a result of the  $\text{Li}^+/\text{H}^+$  exchange during acid treatment [18]. The XRD pattern of PIP showed a very low peak intensity because of the reduced crystallinity, and a change in crystal structure was observed compared with that of the pristine LIP. We expected that the Fe was dissolved from LIP by the acid treatment and that its crystal structure was altered.

**Table 2**

Chemical compositions and crystal structures of the pristine lithium metal compounds, as obtained by AAS and XRD analysis.

Sample	Molar ratio of Li: metals	Crystal structure
LMO	Li:Mn = 1 : 1.83	Spinel
LMNCO	Li: Mn: Ni: Co = 1 : 0.82 : 0.9 : 0.8	Spinel
LCO	Li: Co = 1 : 0.95	Layered
LIP	Li: Fe = 1 : 1.07	Olivine

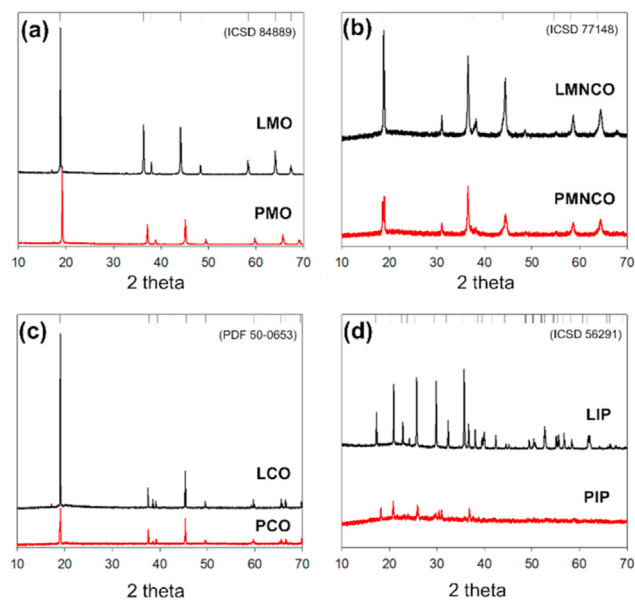


Fig. 1. XRD patterns of the pristine and protonated lithium metal compounds.

### 3.2. Deuterium exchange characteristics of lithium and protonated lithium metal compounds

The exchange reactions between hydrogen present in the protonated lithium metal compounds and deuterium in the aqueous solution were analyzed because deuterium can provide useful information for understanding the behaviors of hydrogen isotopes and predicting tritium behavior. Lithium metal compound or protonated lithium metal compound was suspended in deuterated water (10 wt%  $\text{D}_2\text{O}$ ), and the reduction of the additionally introduced deuterium in the deionized water (9.986 mmol/g) was quantified by FT-IR analysis after the reaction was allowed to equilibrate for 24 h (Table 3). By considering the added amount of the metal compounds in deuterated water, the amount of bound deuterium on the metal compounds was estimated.

The protonated lithium metal compounds were found to adsorb greater amounts of deuterium than the pristine lithium metal compounds (Table 3). The amounts of deuterium retained in protonated lithium metal compounds were 1.25–1.92 mmol/g, which are more than twice that bound to the pristine protonated lithium metal compounds (0.51–0.83 mmol/g). The  $K_d$  values of deuterium

**Table 1**

Chemical composition (wt%) of pristine and protonated lithium metal compounds, as obtained by AAS analysis after acidic digestion.

Sample	Before acid treatment (wt%)	After acid treatment (wt%)
LMO	Li (4.6%), Mn (68.8%)	Li (0.5%), Mn (66.2%)
LMNCO	Li (3.3%), Mn (21.51%), Ni (22.4%), Co (25.25%)	Li (1.8%), Mn (22.1%), Ni (24.4%), Co (27.4%)
LCO	Li (8.3%), Co (60.8%)	Li (7.7%), Co (74.7%)
LIP	Li (4.9%), Fe (42.3%)	Li (0.7%), Fe (26.7%)

**Table 3**

Partitioning of deuterium into the pristine and protonated lithium metal compounds (20 mg/g) after equilibration of reactions at 25 °C for 24 h (initial  $^2\text{H}$  concentration: 9.986 mmol/g).

Sample	Residual $^2\text{H}$ in water (mmol/g)	$^1\text{Bound } ^2\text{H}$ (mmol/g)	$K_d$ (g/g)
LMO	9.976 ± 0.003	0.51 ± 0.15	0.05
LMNCO	9.975 ± 0.004	0.55 ± 0.20	0.06
LCO	9.970 ± 0.005	0.83 ± 0.27	0.08
LIP	9.975 ± 0.004	0.58 ± 0.21	0.06
PMO	9.960 ± 0.008	1.33 ± 0.42	0.13
PMNCO	9.948 ± 0.006	1.92 ± 0.32	0.19
PCO	9.959 ± 0.008	1.36 ± 0.40	0.14
PIP	9.961 ± 0.012	1.25 ± 0.54	0.12

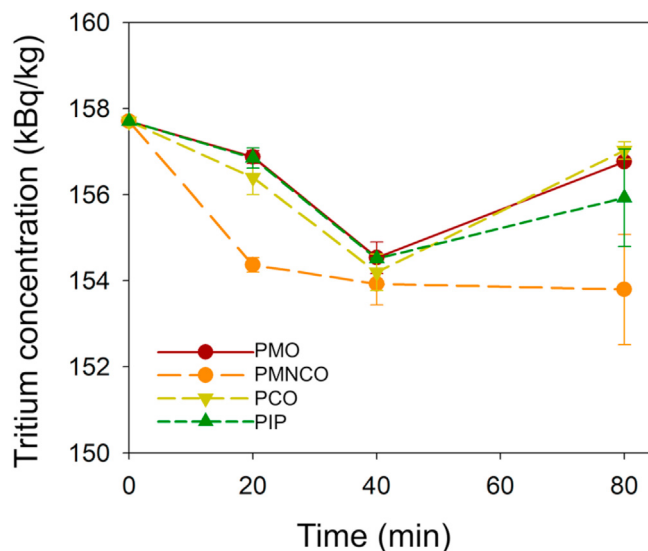
<sup>1</sup> Bound deuterium per gram of samples.

against the pristine and protonated lithium metal compounds were also calculated. The  $K_d$  values of the protonated lithium metal compounds (0.05–0.08 g/g) were slightly higher than those of the non-protonated lithium metal compounds (0.12–0.19 g/g), indicating the increased affinity of the compounds for deuterium after acid treatment. Because  $\text{Li}^+$  ions in the lithium metal compounds can be exchanged with  $\text{H}^+$  ions in acidic solutions, we speculated that the  $\text{Li}^+$  is exchangeable with  $\text{D}^+$  produced by autodissociation of deuterated water or by the catalytic dissociation of  $\text{OD}^-$  ions by the metal oxide [13]. The exchanged amounts of  $\text{Li}^+$  in the compounds with the  $\text{D}^+$  were calculated based on the chemical formulas of the lithium metal compounds, and most lithium metal compounds showed similar amounts of  $\text{D}^+/\text{Li}^+$  exchange which was in the range of 0.9–1.5 mmol/mol. Meanwhile, both  $\text{Li}^+$  and  $\text{H}^+$  ions in the protonated lithium metal compounds are also speculated to be exchangeable with the  $\text{D}^+$  ions in the deuterated water. The  $\text{H}^+$  ions in protonated manganese oxide have been previously reported to form hydrogen bonds with oxygen atoms in the spinel crystal lattice, whereas  $\text{Li}^+$  ions in spinel-structured  $\text{LiMn}_2\text{O}_4$  have been reported to form stable covalent bonds with lattice oxygen by sharing electrons [18,26,27]. In this regard, the  $\text{H}^+$  ions in the protonated lithium metal compounds are more readily exchangeable with hydrons than the  $\text{Li}^+$  in the compounds; thus, the protonated lithium metal compounds tended to adsorb more deuterium in water than the lithium metal compounds.

Among various protonated lithium metal compounds, the PMNCO led to the greatest reduction of the deuterium concentration in water. The amount of D retained in PMNCO was 1.92 mmol/g, which is greater than that bound to PMO (1.33 mmol/g) or PCO (1.36 mmol/g) (Table 3). The  $K_d$  value of the PMNCO was found to be 0.19 (g/g), which is slightly higher than those of the other protonated lithium metal compounds (0.12–0.14 g/g). The deuterium retention and  $K_d$  analysis results imply that the PMNCO has a higher affinity to deuterium than other protonated and pristine lithium metal compounds. Furthermore, the protonation of lithium metal compounds was determined to be beneficial for exchanging the heavier hydrogen isotopes. Subsequent experiments using tritiated water were therefore conducted with the protonated lithium metal compounds for minimizing the generation of radioactive wastes.

### 3.3. Tritium exchange characteristic of protonated lithium metal compounds

To analyze the tritium exchange characteristics of protonated lithium metal compounds, we observed the changes in tritium concentration in light water (initial concentration: 157.7 kBq/kg) as a function of the reaction time after mixing the protonated lithium metal compounds with the solution (Fig. 2). The tritium concentration in the aqueous solution continuously decreased to ~154 kBq/kg during the first 40 min. In the case of PMO, PCO, and PIP, the



**Fig. 2.** Time-dependent changes in radioactivity of tritiated water after reaction with the protonated metal compounds (initial tritium concentration: 157.7 kBq/kg, solid/liquid ratio: 20 mg/g).

concentration of tritium increased again after reaching the lowest tritium concentration at 40 min. Koyanaka et al. have reported that protonated manganese oxide reduced the tritium concentration in light water during the first ~20 min of the reaction and that the tritium concentration subsequently recovered close to its initial concentration [13]. They assumed that the  $\text{T}^+$  ions that replaced  $\text{H}^+$  ions in the protonated manganese oxide transported slowly in the spinel crystal structure and induced tritium reduction in aqueous solution, but that the tritium concentration reached equilibrium over time [13].

When the tritiated water was reacted with the PMNCO, the reduced tritium concentration in the aqueous medium was maintained even after 40 min, unlike the behavior observed with the other protonated lithium metal compounds. To confirm whether the adsorbed tritium could be retained in the protonated lithium metal compound over time, the tritium concentration in the aqueous medium was observed after the reaction was allowed to equilibrate for 24 h (Table 3). In the case of PMO, PCO, and PIP, the tritium concentration in the solution recovered to near the initial concentration after equilibration. By contrast, the reduced radioactivity of the tritiated water reacted with PMNCO was maintained even after equilibration for 24 h. The amount of tritium retained in PMNCO was found to be 163.9 Bq/g, which is almost twice that bound to the PMO (69.9 kBq/g) or PCO (75.1 kBq/g) (Table 4).

The  $K_d$  values of tritium against the protonated lithium metal compounds were also calculated. The  $K_d$  value of the PMNCO was found to be 1.06, which is almost twice the  $K_d$  values of the other protonated lithium metal compounds. For comparison, previously

**Table 4**

Partitioning of tritium into the protonated lithium metal compounds (20 mg/g of tritiated water) after equilibration of reactions at 25 °C for 24 h (initial  $^3\text{H}$  concentration: 157.7 kBq/kg).

Sample	Residual $^3\text{H}$ in water (kBq/kg)	$^1\text{Bound } ^3\text{H}$ (Bq/g)	$K_d$ (g/g)
PMO	156.3 ± 0.8	69.9 ± 0.4	0.45
PMNCO	154.4 ± 0.9	163.9 ± 1.0	1.06
PCO	156.2 ± 0.4	75.1 ± 0.2	0.48
PIP	155.9 ± 0.1	87.3 ± 0.1	0.56

<sup>1</sup> Bound tritium per gram of protonated lithium metal compound.

reported  $K_d$  values of tritium for soil media are approximately 0.1–0.2 [24]. The high  $K_d$  values of the protonated lithium metal compounds used in the present study imply high tritium affinity. Moreover, the  $K_d$  values of tritium (0.45–1.06 g/g) were higher than that of deuterium (0.13–0.19 g/g) against protonated lithium metal compounds, indicating higher affinity of the compounds for tritium than deuterium. It is expected that the isotope effect of hydrogen enabled the protonated lithium metal compounds to entrap heavier hydrogen isotopes rather than light proton, and the heaviest hydrogen isotope, tritium, seems to have the highest tendency to be retained in the compound.

Although both PMNCO and PMO have a spinel structure and Mn component, the PMNCO can entrap more tritium or deuterium than PMO. Because the PMNCO contains Ni and Co in addition to Mn, such metal components may influence the tritium exchange and retention. The  $H^+/T^+$  exchange between  $MHPO_4$  ( $M = Mn^{2+}, Mg^{2+}, Sr^{2+}$ ) and HTO vapor has been reported to be promoted by more electronegative metal components ( $M$ ) [28]. Because Ni and Co are more electronegative than Mn, the doping of the spinel structure with Ni and Co might increase the reactivity of the  $H^+$  site for  $H^+/T^+$  exchange, although a comprehensive study is needed to clarify this issue.

We observed a reduction in the percentage (%) of tritium in the water (157.7 kBq/kg) by varying the amounts of the protonated lithium metal compound added after the reaction was allowed to equilibrate for 24 h (Fig. 3). The reduction of tritium increased with increasing amount of the protonated lithium metal compound in the dispersion, as expected, and the PMNCO exhibited the greatest tritium reduction ( $3.94 \pm 1.25\%$ ) among the investigated protonated lithium metal compounds.

#### 4. Conclusion

The hydrogen isotope exchange characteristics of various protonated lithium metal compounds in tritiated or deuterated water were investigated. The protonated lithium metal compounds were prepared via  $H^+$ -for- $Li^+$  ion exchange by acid treatment of various lithium metal compounds with different crystal structures and metal compositions. The acid-treatment of spinel-structured LMO, spinel-structured LMNCO, and layered LCO provided protonated forms of the metal oxide crystals. By contrast, the crystal structure

of olivine-structured LIP was partially destroyed by dissolution of the metallic components. The protonation of lithium metal compounds enhanced the reduction of the deuterium concentration in water, implying that the  $H^+$  was more readily exchangeable with hydrons in the aqueous solution compared with stably bound  $Li^+$  in the lithium metal compounds. Most of the protonated lithium metal compounds were also able to adsorb tritium in water by  $H^+/T^+$  exchange between the protonated and tritiated water and reached their maximum tritium adsorption within 40 min. Among the various protonated lithium metal compounds, the PMNCO could exchange and retain the largest amount of tritium after equilibration of the reaction. We speculated that the isotope effect of hydrogen enabled the protonated lithium metal compounds to entrap heavier isotopes, such as tritons or deuterons, rather than light protons via the slow transport and stable binding of heavier isotopes in the crystal structures [13]. The spinel structures containing Ni or Co appeared to promote the entrapment of heavier hydrogen isotopes.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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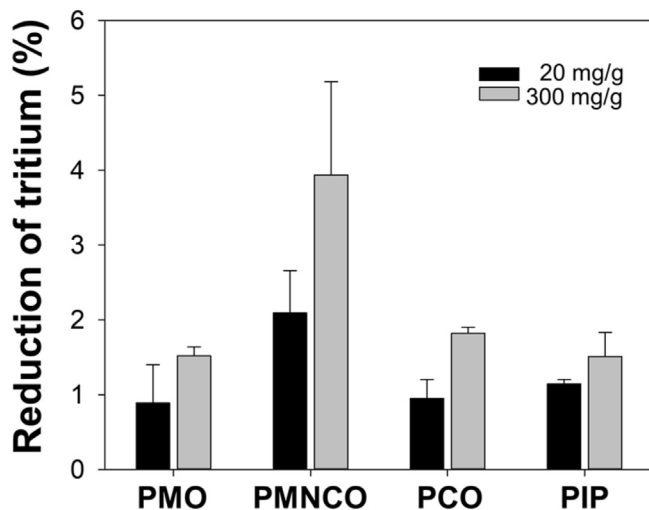


Fig. 3. Reduction of tritium by reaction with protonated lithium metal compounds (20 or 300 mg/g of tritiated water) at 25 °C for 24 h (initial  $^3H$  concentration: 157.7 kBq/kg).

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