Extraction of Lithium from Single-Crystalline Lithium Manganese Oxide Nanotubes Using Ammonium Peroxodisulfate

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HIGHLIGHTS

- Single-crystalline Li$_{1.1}$Mn$_{1.9}$O$_4$ nanotubes were developed for lithium extraction.
- The sorbent showed Li/Mn ratio depletion over adsorption/desorption processes.
- Acid-free extraction minimized the structural change and Mn reduction.
- Acid-free extraction improved the chemical stability and reusability of the sorbent.

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SUMMARY
In this work, a spinel single-crystalline Li$_{1.1}$Mn$_{1.9}$O$_4$ has been successfully synthesized using β-MnO$_2$ nanotubes as the self-sacrifice template. The tubular morphology was retained through solid-state reactions, attributed to a minimal structural reorganization from tetragonal β-MnO$_2$ to spinel Li$_{1.1}$Mn$_{1.9}$O$_4$. The materials were investigated as sorbents for lithium recovery from LiCl solutions, recycled using H$_2$SO$_4$ and (NH$_4$)$_2$S$_2$O$_8$. Li$_{1.1}$Mn$_{1.9}$O$_4$ nanotubes exhibited favorable lithium extraction behavior due to tubular nanostructure, single-crystalline nature, and high crystallinity. (NH$_4$)$_2$S$_2$O$_8$ eluent ensures the structural stability of Li$_{1.1}$Mn$_{1.9}$O$_4$ nanotube, registering a Li$^+$ adsorption capacity of 39.21 mg g$^{-1}$ (~89.73% of the theoretical capacity) with only 0.08% manganese dissolution after eight adsorption/desorption cycles, compared to that of 1.21% for H$_2$SO$_4$. It reveals the degradation of sorbent involves with the volume change, Mn reduction, and Li/Mn ratio depletion. New strategies, based on nanotube adsorbent and (NH$_4$)$_2$S$_2$O$_8$ eluent, can extract lithium ions at satisfactorily high degrees while effectively minimizing manganese dissolution.

INTRODUCTION
The demand for lithium production worldwide has significantly increased in recent years due to the growth of the rechargeable lithium-ion battery market (Li et al., 2018). The sources of lithium are mainly in forms of water resources and ore bodies, such as spodumene, lepidolite, and petalite ores. The grown interest in lithium extraction derived from water resources is attributed to its low cost, natural abundance, and environmental friendliness (Battistel et al., 2020). Great efforts have been devoted to selective recovery of Li$^+$ from water resources, including precipitation (Biswal et al., 2018), evaporative crystallization (Ooi et al., 2017), solvent extraction (Zhang et al., 2020), electrochemical adsorption (Battistel et al., 2020; Du et al., 2016), and ion exchange adsorption (Lin et al., 2019; Wang et al., 2020). The precipitation and evaporative crystallization are limited for processing high concentrated Li$^+$ solutions, which requires a pre-concentration process that entails tedious treatment and large energy consumption. Although the solvent extraction indicates high selectivity of lithium, the use of organic solvents generates significant environmental concerns. Electrochemical adsorption, based on the redox reactions of electrodes, has attracted increasing attention (Pasta et al., 2012; Trócoli et al., 2017). In this technique, the materials are regenerated using an external power source, which avoids the use of chemicals for adsorbent regeneration; however, the method exhibits irreversible electrochemical reactions and limited lithium productions due to low energy efficiency (Pasta et al., 2012).

Lithium-ion sieve technology represents a cost-effective green method, based on functional adsorbents capturing of lithium ions from the brines (Paranthaman et al., 2017; Tang et al., 2020; Xu et al., 2016). Among various materials, spinel-type lithium manganese oxides Li$_x$(Mn$^{II}$Mn$^{IV}$)O$_4$ or LMOs attract more attention from academic researchers and, more recently, from the industry due to feasible production, excellent selectivity, and high lithium uptake capacity (Luo et al., 2016). A lithium-ion sieve is derived from the extraction of Li$^+$ from spinel-type LMOs (Luo et al., 2016). In general, mild acids are employed for an ion exchange between Li$^+$ and H$^+$ yielded to a hydrogen manganese oxide (HMO) (Choi et al., 2020; Hong et al., 2018). However, the promise of LMOs has been hampered by its low chemical stability in the acidic environment (Wang et al., 2020). It is known that the Mn$^{III}$ in the LMOs can undergo a disproportionation reaction and turn into Mn$^{II}$ and Mn$^{IV}$ upon delithiation (Hayashi et al., 2017). New strategies, based on nanotube adsorbent and (NH$_4$)$_2$S$_2$O$_8$ eluent, can extract lithium ions at satisfactorily high degrees while effectively minimizing manganese dissolution.

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et al., 2016). The collapse of the spinal structure, triggered by the MnII/MnIV dissolution, degrades the performance and reusability of the sorbent. Therefore, the acidic treatment poses a persistent challenge for LMO implementations of lithium exploitations.

The interest in applications of nanostructured sorbents for lithium extraction is attributed to its high surface area and high adsorption capacity (Du et al., 2016; Kamran et al., 2019; Luo et al., 2016). However, relatively poor stability has been achieved. The adsorption performance strongly depends on the morphology, porosity, and crystalline structure of the material (Xu et al., 2016). One-dimensional nanomaterial with enlarged surface area and accessible extraction-desorption sites is promising for lithium recovery (Moazeni et al., 2015). The nanostructured network facilitates favorable ion transportation, thus allowing high Li+ uptake capacity and fast recovery kinetics (Tang et al., 2013; Wu and Zhao, 2011). It has been demonstrated that single-crystalline material boosts efficient and reversible lithiation/delithiation processes due to its well-defined geometry, short Li+ ions diffusion length, and perfect crystallization (Ding et al., 2011). In this study, we synthesized a single-crystalline LMO nanotube, with a composition of Li1.1Mn1.9O4, for the selective recovery of Li+ from LiCl solutions and simulated brines. The reusability and adsorption performance of LMO nanotubes was ensured using ammonium persulfate ((NH4)2S2O8) as the eluent.

RESULTS

Figure 1A shows a typical Scanning Electron Microscope (SEM) image of LMO nanotubes prepared by a template-engaged synthesis using β-MnO2 nanotubes as the precursor. The LMO nanotubes exhibited a length and a width in a range of 0.5–2 μm and 70–200 nm, respectively. The interior hollow structure of LMO nanotubes was observed by Transmission electron microscope (TEM) (Figures 1B and 1C). The formation of β-MnO2 templates (Figures S1A and S1B, Supplemental Information), based on the hydrothermal process, encompasses through a nucleation-dissolution-anisotropic growth-recrystallization mechanism. The growth of β-MnO2 tubular structures involves the dissolution and recrystallization of γ-MnOOH as intermediates. The tips of β-MnO2 templates exhibit a sharp boundary as the material undergoes a phase transition from the intermediates to β-MnO2, leading to a tubular nanostructure (Figures S1C and S1D, Supplemental Information). This morphology is effectively maintained during the subsequent solid-state reaction (Figure 1B). The aspect ratio of nanotubes is increased, indicated that the tubes slightly swell in the direction perpendicular to the tube axis through the template-engaged transformation process. High-resolution TEM results reveal a single-crystalline structure of LMO nanotube, with an inner and outer diameter of 48 and 70 nm, respectively (Figure 1C). The composition and crystal structure of obtained LMO nanotubes were analyzed by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) and X-ray Diffraction (XRD) characterizations. The nanotubes demonstrated a well-crystallized cubic spinel structure with the Fd3m symmetry (Figure S2, Supplemental Information). The lattice constant is calculated to be 8.239 Å, which is slightly smaller than that of the literature value (8.248 Å, JCPDS No. 35–0782), implying that partial manganese sites might be occupied by lithium in the spinel lattice. The assumption is supported by ICP-OES measurements. The results showed that the atomic ratio of Li:Mn is 0.578, indicating that a lithium-rich phase of Li1.1Mn1.9O4 is obtained by the reaction between nanotube templates and LiOH at the high temperature. The extra Li+ in interstitial sites of the lithium-rich manganese oxide improves the structural stability and allows higher Li+ uptake capacity (Bajestani et al., 2019; Chitrakar et al., 2001; Xiao et al., 2013). It is found that the Brunauer-Emmett-Teller (BET) surface area of LMO nanotubes is 121.3 m² g⁻¹ (Figure 2), with an average pore size around 50 nm determined by the Barrett-Joyner-Halenda method, which is in good agreement with TEM analysis.
To understand solid-state reactions, we investigated the XRD patterns for the β-MnO2 nanotube and the calcined products, obtained at 500, 600, and 700°C respectively (Figure 3). The diffraction peaks of nanotube templates are indexed for the tetragonal structure of β-MnO2 (JCPDS 24–0735, space group P42/mnm) without any impurity peaks. Lithium ions enter the square channels of tetragonal β-MnO2 via solid-state reactions. The reduction of MnIV to MnIII leads to the lattice expansion owing to the larger radius of MnIII than MnIV phase, accompanied by the formation of LiO4 tetrahedra and new MnO6 octahedra. As XRD results showed, the calcination triggers the reorganization of structure owing to the strongest diffract peak corresponding to (110) reflections of β-MnO2 disappeared. The transformation is facilitated by the high mobility of Li+ ions at elevated temperatures (Lu et al., 2019). While LMO500 and LMO600 show the presence of α-Mn2O3 phase, an undistorted cubic bixbyite with Ia3 symmetry (Supplemental Information); the reaction at 700°C complete phase transformation from tetragonal β-MnO2 to spinel Li-rich structure. The SEM images of the products prepared at different temperatures showed the nanotube morphology is preserved (Figure S4, Supplemental Information). Despite the impurities were identified at the surface of LMO nanotubes calcined at 500°C (Figures S4A and S4D), the materials show a uniform tubular morphology upon increasing the temperature. The dimension of LMO nanotubes does not change evidently over the solid-state reaction (Figures S4A–S4C). It has been suggested that the tetragonal-to-cubic transformation requires a cooperation jump to a nearest-neighbor site of half the cation array, followed by an adjustment of the Mn-O distances to convert the tetragonal anion packing of rutile to the cubic close packing of anions in the spinel structure (David et al., 1984). The adjustment sustained a minimal reorganization of structure in the tetragonal precursor, generated a more stable spinel LMO framework with a higher symmetry than that of the nanotube templates. Therefore, the tubular nanostructure and high crystallinity of the precursor were preserved through solid-state reactions.

Spinel LMO nanotubes, prepared by β-MnO2 nanotube and LiOH at 700°C, were selected for Li+ adsorption/desorption tests followed by the experimental procedure shown in Figure S5 (Supplemental Information). Figure 4A presents the elution curves, accompanied by manganese dissolution, for LMO nanotubes delithiated by 0.5 M H2SO4 and (NH4)2S2O8. The results showed that the (NH4)2S2O8-eluted LMO nanotubes exhibited significantly low manganese dissolution and slightly decreased Li+ recovery kinetics, as compared to H2SO4-eluted LMO. To elucidate the advantages of single-crystalline nano-tubular structure, we tested the extraction performance of commercial LiMn2O4 materials purchased from Aldrich (Figures S6A and S6B, Supplemental Information). The commercial LMO particles exhibit moderate kinetics and low Li+ uptake capacity (Figure S6C, Supplemental Information), whereas Li+ uptake capacity of LMO nanotubes was initially high and then steadily reached for an equilibrium. The (NH4)2S2O8-eluted LMO nanotubes showed low manganese dissolution due to the hydrolysis of S2O82−, where the peroxy bond breaks into SO42− free radicals (Equation 1) (Marthi and Smith, 2019). The SO42−/SO32− transformation (Equation 2)
has a high positive reduction potential ($E^\prime = +2.43$ V) compared to Mn$^{III}$/Mn$^{II}$ ($E^\prime = +1.54$). As a result, SO$_4^{2-}$ exhibits a higher affinity to accept electrons than Mn$^{II}$. Therefore, SO$_4^{2-}$ free radicals replace Mn$^{III}$ as an electron acceptor in the Li$_x$(Mn$^{III}$Mn$^{IV}$)O$_4$ framework, inhibiting the reduction of Mn$^{III}$.

\[
\begin{align*}
S_2O_2^{2-} &\rightarrow 2SO_4^{2-} & \text{(Equation 1)} \\
2SO_4^{2-} + 2H_2O &\rightarrow 2SO_3^{2-} + 2H^+ + H_2O_2 & \text{(Equation 2)} \\
2H_2O_2 &\rightarrow 2H_2O + O_2 & \text{(Equation 3)} \\
Li_x(Mn^{III}Mn^{IV})O_4 + xH^+ &\leftrightarrow H_x(Mn^{III}Mn^{IV})O_4 + xLi^+ & \text{(Equation 4)}
\end{align*}
\]

While $H^+$ acts as an acid extracting Li$^+$ from LMO nanotubes (Equation 3), the dissolution of manganese could be alleviated due to the generation of $O_2$ as an oxidant (Equation 4) (Ogino and Oi, 1996). In contrast to commercial LiMn$_2$O$_4$, surface disproportionation might occur in LMO nanotubes due to extra Li$^+$ in the interstitial sites (Ariza et al., 2006). A hybrid mechanism was involved for Li$^+$ extraction in LMO nanotubes, containing ion exchange behavior between Li$^+$ and $H^+$ and redox extraction of Li$^+$. The results of repeated lithium adsorption/desorption tests are shown in Figure 4B. Lithium recovery tests were executed in LiCl solutions using eluted LMO nanotubes. Then, the sorbent was placed in 0.5 M $H_2SO_4$ or (NH$_4$)$_2$S$_2$O$_8$ to regenerate lithium from adsorbed samples. The manganese dissolution in the nanotube matrix was higher in the first cycle, especially for the $H_2SO_4$-treated samples, due to insufficient transformation, Mn$^{III}$ disintegration, and interplanar distance contraction caused by the acidic attack (Gao et al., 2019). The theoretical Li$^+$ extraction capacity is 43.70 mg g$^{-1}$ based on the composition of Li$_1.1$Mn$_{1.9}$O$_4$. The (NH$_4$)$_2$S$_2$O$_8$-eluted LMO nanotubes registered a recovery capacity of 39.21 mg g$^{-1}$ with a capacity retention of 86.73% after regeneration, whereas the capacity retention of $H_2SO_4$-eluted LMO is only 69.67%. Meanwhile, the recovery capacity of $H_2SO_4$-eluted LMO was sharply decreased during adsorption/desorption cycling, compared to LMO nanotubes eluted by (NH$_4$)$_2$S$_2$O$_8$. After the eight cycles, LMO nanotubes obtained from (NH$_4$)$_2$S$_2$O$_8$ eluent exhibited a recovery capacity of 23.96 mg g$^{-1}$ and corresponding Mn dissolution of 0.12%, while $H_2SO_4$-eluted LMO nanotubes showed a recovery capacity of 10.96 mg g$^{-1}$ and $H_2SO_4$-eluted commercial LMO failed to function (Figure S6D, Supplemental Information).

XRD patterns of pristine LMO and LMO nanotubes, eluted by $H_2SO_4$ and (NH$_4$)$_2$S$_2$O$_8$, after cycling tests were shown in Figure 4C. It is observed that the spinel structure of LMO nanotubes was preserved for both $H_2SO_4$-eluted and (NH$_4$)$_2$S$_2$O$_8$-eluted LMO nanotubes. As the peak shift toward higher 2$\theta$ values is observed upon delithiation, retention of the spinel structure indicates lithium desorption proceeds...
Rietveld refinements were used to analyze the XRD results of H$_2$SO$_4$-eluted and (NH$_4$)$_2$S$_2$O$_8$-eluted LMO nanotubes (Figures 4D and 4E). LMO nanotubes, eluted by 0.5 M H$_2$SO$_4$ and (NH$_4$)$_2$S$_2$O$_8$, exhibit a lattice parameter of 8.032 and 8.054 Å, respectively, indicating a larger volume change for H$_2$SO$_4$-eluted LMO nanotubes (Table 1). While the pristine LMO showed a Li-rich spinel structure after solid-state reactions, the ratio of Li/Mn is reduced due to Mn dissolution after eight adsorption/desorption cycles (Table 1). It has been known that adequate Mn$^{III}$/Mn$^{IV}$ ions in the spinel structure are necessary to maintain the ideal cubic dense packing state of O atoms in each layer, forming a Mn$_2$O$_4$ skeleton which is favorable for Li$^+$ diffusion (Figure 4F) (Ben et al., 2017). The Li$^+$ extraction at the 8a position of the LMO through the path of 8a→16c→8a. The Jahn-Teller effect may occur during the adsorption/desorption process that the repeated insertion/extraction of Li$^+$ causes the deformation and even collapse of the spinel structure (Ragavendran et al., 2017).

Figure 5A showed that X-Ray Photoelectron Spectroscopy (XPS) spectra of Mn 2$P_{1/2}$ and Mn 2$P_{3/2}$ for pristine LMO and LMO nanotubes, eluted by H$_2$SO$_4$ and (NH$_4$)$_2$S$_2$O$_8$. The shift of binding energy is attributed to the lattice distortion of manganese-oxygen bonds (Qian et al., 2020). The valence analysis was performed by deconvolutions of Mn 2$P_{3/2}$ spectra (Figure 5B). The results indicated that the ratios of Mn$^{4+}$/Mn$^{3+}$ on the surface are 51.0%:49.0%, 44.9%:55.1%, and 46.8%:53.2% for pristine LMO, H$_2$SO$_4$-eluted, and (NH$_4$)$_2$S$_2$O$_8$-eluted LMO nanotubes, respectively (Table 1). While eluted LMO nanotubes exhibit an increase of Mn$^{3+}$, (NH$_4$)$_2$S$_2$O$_8$-eluted LMO nanotubes showed higher valence state of Mn compared to H$_2$SO$_4$-eluted LMO nanotubes. The reduction of Mn triggered dissolutions of Mn$^{2+}$ in acid solutions during the extraction process (Gao et al., 2018). It is suggested that as the average valence state of Mn decreased lower than +3.5, the cubic crystal changes to tetragonal, while the tetragonal phase showed irreversible transformations of Li$^+$ adsorption/desorption (Abuzeid et al., 2018). The improved recovery performance of LMO nanotubes is attributed to higher chemical stability and less volume changes for the acid-free processing.

The acid-free method was employed for Li$^+$ recovery from simulated brines. (NH$_4$)$_2$S$_2$O$_8$-eluted LMO nanotubes exhibited a high selectivity of Li$^+$ from the brine, containing Li$^+$, Na$^+$, K$^+$, and Mg$^{2+}$ ions under the
same batch condition (Figure S7A Supplemental Information). The concentration of cations plays an important role in the adsorption behavior of nanotubes. Considering the extremely unbalance ratio was detected in salt lakes, the adsorption capacity of (NH4)2S2O8-eluted LMO nanotubes was tested using brines with different Li+:Na+ ratios. As shown in Figure S7B (Supplemental Information), (NH4)2S2O8-eluted LMO nanotubes retain 88.32% of adsorption capacity with good Li+ recognition ability when Li+:Na+ ratio is increased from 1:1 to 1:10. Further increase of the brine concentrations results in the presence of white crystals, ascribed to the unabsorbed salts (Figure S8, Supplemental Information). The adsorption performance was briefly summarized and compared with previous studies (Table S1, Supplemental Information). The results demonstrated that single-crystalline nanotubes deliver excellent adsorption capacity and the highest extraction efficiency with respect to the theoretical capacity of adsorption. Thus, the acid-free strategy is promising for practical applications of lithium extraction.

DISCUSSION
With the surging demand for lithium, it is necessary to develop new technologies for lithium extraction with high efficiency and good reusability. In this work, we developed a new strategy for nano-extraction of lithium, based on single-crystalline LMO nanotubes recycled by (NH4)2S2O8 as an eluent. The promising Li+ recovery performance of LMO nanotubes is attributed to their novel architecture and single-crystalline structure. The LMO nanotubes obtained via template-engaged reaction can serve as channels for lithium-ion adsorption/desorption, whereas the hollow nanostructure of spinel LMO may act as reservoirs for the lithium uptake. The limitation of internal pore diffusion could be overcome by the tubular morphology, consequently leading to a sufficient adsorbent-solution interface to absorb Li+ and promote rapid ion transportation. While nano-sized holes in LMO nanotubes can supply facile transport channels with short length for lithiation, a single-crystalline structure can reduce the transport resistance of lithium ions. On the other hand, LMO materials suffer from performance degradations due to manganese dissolutions and irreversible volume changes in the conventional acidic elution process. (NH4)2S2O8 eluent ensures the structural stability of LMO nanotubes by improving the reversibility of Li+ recovery and buffering the volume change, attributed to Jahn-Teller effects. The method developed in this investigation can be used for the synthesis and modifications of LMO materials for various applications such as battery recycling and lithium-ion sieve fabrications.

Overall, we successfully demonstrated a nano-extraction approach, based on LMO nanotubes as the adsorbent and (NH4)2S2O8 as the eluent. Spinel LMO nanotubes were synthesized via a template-engaged reaction using β-MnO2 nanotubes as the precursor, in which the tubular morphology and single-crystal characteristics of LMO nanotubes can be preserved due to minimal structure reconstruction during the phase transformation. As the sorbent for lithium recovery, the LMO nanotubes exhibited favorable extraction performance, which may be attributed to their unique tubular nanostructures, single-crystalline nature, and high crystallinity. The manganese dissolution in the acidic environment has been overcome by using (NH4)2S2O8 for lithium recovery. (NH4)2S2O8 eluent improves recovery performance and cycling stability of LMO nanotubes compared to that eluted by H2SO4. The acid-free extraction ensures the reusability, selectivity, and recovery properties for spinel LMO materials.

Table 1. Rietveld Refinement Results, Mn Valence, and Li:Mn Ratio for Different Materials

|                          | Pristine LMO | LMO Recycled by H2SO4 | LMO Recycled by (NH4)2S2O8 |
|--------------------------|--------------|------------------------|---------------------------|
| a (Å)                    | 8.239        | 8.032                  | 8.054                     |
| V (Å3)                   | 559.27       | 518.17                 | 522.44                    |
| Crystallite size (nm)    | 12.52        | 15.17                  | 14.72                     |
| Rwp (%)                  | 2.83         | 3.48                   | 3.12                      |
| Mn4+ (%):Mn3+ (%)        | 51.0:49.0    | 44.9:55.1              | 46.8:53.2                 |
| Li:Mn ratio              | 0.578        | 0.513                  | 0.572                     |

Li:Mn ratio was obtained from ICP-OES tests. Mn Valence was analyzed by XPS measurements.
Limitations of the Study

Here, we proposed single-crystalline LMO nanotubes, synthesized by a template-engaged method, for lithium extractions. The degradation of LMO nanotubes has been overcome using (NH4)2S2O8 as the eluent, which reduced manganese dissolutions and improved capacity retention upon adsorption/desorption processes. The marriage of LMO nanotubes and (NH4)2S2O8 allows 89.73% theoretical capacity of the sorbent in pure LiCl solutions. However, for lithium recovery from real brines, efficiency and adsorption behavior need to be optimized according to in-service conditions. For those containing highly concentrated Na+ and Mg2+, recovery practices should be integrated with pre-treatments, such as filtration, evaporation, and participation.

Resource Availability

Lead Contact
Further information and requests for resources should be directed to the Lead Contact, Kaiyuan Shi (shiky7@mail.sysu.edu.cn).

Materials Availability
The materials that support the findings of this study are available from the corresponding author upon reasonable request.

Data and Code Availability
This study did not generate/analyze data sets/code.

METHODS

All methods can be found in the accompanying Transparent Methods supplemental file.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2020.101768.

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AUTHOR CONTRIBUTIONS

K.S. conceived the idea and managed the project. M.L., J.Y., S.Z., Z.X., and R.C. performed the experiments. K.S. and Z.X. analyzed the results and wrote the paper. All authors discussed the results and contributed to the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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Supplemental Information

Extraction of Lithium from Single-Crystalline Lithium Manganese Oxide Nanotubes Using Ammonium Peroxodisulfate

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**Transparent Methods**

*Preparation of single-crystalline LMO nanotubes*

Spinel-type LMO nanotubes were prepared by β-MnO₂ nanotube templates by a modified hydrothermal process. In this method, MnSO₄·H₂O (40 mmol) and PVP (45 mmol, K30) were dissolved in deionized water (100 mL). Then, 40 mL NaClO₃ (1 M) solution was added to the above solution under continuous stirring. The mixed solution was transferred to a Teflon-lined stainless steel autoclave and heated at 180°C for 10 h. The black precipitate was filtered and washed with deionized water and ethanol, and subsequently dried in a vacuum oven. The as-prepared β-MnO₂ was mixed with LiOH·H₂O at a molar ratio of 1.9:1.1 (with an extra ~5% LiOH·H₂O) and dispersed into 10 mL methanol to form a homogenous slurry, and then dried at the room temperature overnight. The mixture was calcined in a range of 500-700 °C for 10 h to obtain spinel LMO nanotubes.

*Characterization of Materials*

The crystallographic structure was studied by the X-ray diffraction (XRD) method, operated on a powder diffractometer (NicoletI2, monochromatized CuK-α radiation). The obtained patterns were refined by the TOPAS program using the Rietveld method, with ICSD crystallographic information as references for the refinements(Majzoub and Rönnebro, 2012). The BET specific surface area and pore size distribution were acquired using the nitrogen adsorption/desorption method by Quantachrome Autosorb-1 equipment. The microstructure was investigated by Hitachi SU5000 scanning electron microscope (SEM) and FEI Tecnai Osiris Transmission electron microscopy (TEM). The concentration of metal ions in the solution was determined by an inductively coupled
plasma-optical emission spectroscopy (ICP-OES, Thermo Jarrell Ash IRIS Advantage). The surface chemistry and the valence state of Mn were studied using X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha).

**Lithium extraction/recovery tests**

Lithium adsorption/desorption performance was studied in a batch system as shown in Figure S5. The obtained powders were firstly delithiated in the eluent until the extraction of lithium reached equilibrium. The lithium recovery experiments were conducted in 0.1 M LiCl solutions at 60°C. The pH of LiCl solutions was adjusted to 8 using 1 M LiOH. The recovery of lithium was carried out by stirring 1 g HMO powders in 40 ml of lithium solutions for 4 h. For the desorption tests, the sorbent was stirred in a 0.5 M H$_2$SO$_4$ or (NH$_4$)$_2$S$_2$O$_8$ solution for 4 h. Sorbent–sorbate mixture was analyzed after centrifuged at 3500 rpm for 10 min, followed by washing with DI water to remove the residues. The Li$^+$ selectivity tests were carried out using 1 g (NH$_4$)$_2$S$_2$O$_8$-eluted LMO nanotubes in 40 mL in simulated brines. The brines contain 0.05 M LiCl, KCl and MgCl$_2$, and NaCl in different concentrations of 0.05-0.5 M. The concentrations of Li$^+$ and coexisting cations in all solutions were determined at intervals by the ICP-OES. The adsorption capacity was calculated by $q_e = \Delta C * V / m$, where $\Delta C$ is the change of Li$^+$ concentration (mg L$^{-1}$); $V$ is solution volume (L); and $m$ is sorbent mass (g), respectively. The adsorption capacity was reported based on the average value calculation for three samples.
Figure S1 A, B) SEM and C, D) TEM images of $\beta$-MnO$_2$ nanotube templates, obtained from a hydrothermal process, at different magnifications. The arrows in (D) show the tip with an interior hollow structure of individual tubes. Related to Figure 1.
Figure S2 Rietveld refinement results of LMO nanotubes, prepared by a solid-state reaction between β-MnO$_2$ nanotube templates and LiOH·H$_2$O at 700 °C for 10 h. The pattern was refined using a single-phase model with the $Fd3m$ symmetry; in this structure, lithium, manganese and oxygen reside on the 8a (tetrahedral), 16d (octahedral), and 32e Wyckoff sites, respectively. The instrumental resolution function was determined by fitting the XRD pattern of a standard powder sample LaB$_6$ (Britto and Kamath, 2014). Related to Figure 1.
Figure S3 Crystal structure of $\alpha$-Mn$_2$O$_3$ (Bixbyite JCPDS 41-1442, $Ia-3$ structure), formed by a solid-state reaction between $\beta$-MnO$_2$ templates and LiOH·H$_2$O within a range of 500-600 °C, in the view of A) atom and B) polyhedral model. Related to Figure 3.
Figure S4 SEM images of the products derived from a solid-state reaction between β-MnO$_2$ nanotube templates and LiOH·H$_2$O at different temperatures for 10 h: A) 500 °C, B) 600 °C, C) 700°C, and D) the magnified view of A). The arrows in (D) show the impurities corresponding to α-Mn$_2$O$_3$ phase (JCPDS 41-1442). Related to Figure 3.
Figure S5 Scheme of experimental procedures for LMO nanotube synthesis and Li$^{+}$ adsorption/desorption tests. Related to Figure 4.
Figure S6 A, B) SEM images of commercial LiMn$_2$O$_4$ materials at different magnifications and C) elution test and D) regeneration test results of Li extraction for commercial LiMn$_2$O$_4$ materials, delithiated using 0.5 H$_2$SO$_4$. The tests were carried out at the temperature of 60°C and pH of 8, adjusted by 1M LiOH. The spinel LiMn$_2$O$_4$ materials from Sigma-Aldrich (Stock# 725129) were investigated because of its wide availability. SEM image shows the materials are heterogeneous with a broad size distribution in the micron-size. The initial ($C_0$) and final ($C_1$) concentrations of Li$^+$ solutions were measured by ICP-OES tests. The Li$^+$ recovery capacity ($Q$) was obtained based on the change of Li$^+$ concentration. Related to Figure 4.
Figure S7 Recovery behavior of (NH₄)₂S₂O₈-eluted LMO nanotubes in simulated brines:

A) competitive cation uptakes tested at 0.05 mol L⁻¹ Li⁺, Na⁺, K⁺, and Mg²⁺ and B) adsorption performance at different Na⁺:Li⁺ ratios. Related to Figure 4 and Table 1.

For practical applications of lithium recovery from brines, Li⁺-containing mother liquors may carry various cations, such as Na⁺, K⁺, and Mg²⁺ ions, etc (Marthi and Smith, 2019; Ryu et al., 2016). Therefore it is essential to investigate the influence of coexisting ions on the adsorption performance of LMO nanotubes. The selectivity tests were carried out using simulated brines containing LiCl, NaCl, KCl and MgCl₂. 1 g (NH₄)₂S₂O₈-eluted LMO nanotube was dispersed in 40 ml of the brine at 60°C for 4 h. The concentrations of each ion were measured using ICP-OES before and after extraction tests. Simulated brines exhibited lower Li⁺ uptake capacity compared to LiCl solutions, indicating Li⁺ adsorption was regulated by cation concentrations. (NH₄)₂S₂O₈-eluted nanotubes showed a high selectivity of Li⁺ as the adsorption capacity of Li⁺ is two orders higher, compared to that of Na⁺, K⁺, and Ca²⁺ (Figure S7A). The Li⁺ adsorption performance was evaluated at different Na⁺ concentrations. The results indicated that (NH₄)₂S₂O₈-eluted LMO nanotubes remained 88.32% of Li⁺ adsorption capacity when the ratio of Na⁺:Li⁺ was increased to 10:1 (Figure S7B).
Figure S8 Nanotube adsorbents after recovery tests using A) 0.05 and B) 0.1 mol L\(^{-1}\) Li\(^+\), Na\(^+\), K\(^+\), and Mg\(^{2+}\) brines. The tests were carried out at 60°C while stirring at 200 rpm for 1 h. The presence of white crystals indicated that the washing step is insufficient to remove salts, which is not adsorbed by the sorbent in simulated brine. Related to Figure 4 and Table 1.
Table S1 Comparison of the extraction strategy developed in this work with other studies. Related to Figure 4.

| Materials | Synthesis method | Sample | Li⁺ concentration (mg/L) | T/pH | Li⁺ uptake (mg/g) | Qₜh (mg/g) | Efficiency (%) | Manganese dissolution | Reference |
|-----------|------------------|--------|--------------------------|------|-------------------|------------|----------------|----------------------|-----------|
| Li₄MnO₄   | solid-phase      | LiCl solution | 69.4 | 30°C/1 0.1 | 40 | 56 | 71 | 1.90% | (Xiao et al., 2015) |
| Li₄MnO₄   | hydrothermal     | LiCl solution | 69.4 | 30°C/1 0.1 | 21 | 38 | 55 | N/A | (Zhang et al., 2010) |
| Li₄MnO₄   | solid-phase      | LiOH solution | 83 | 25°C/N | 32 | 68 | 47 | 4.00% | (Qian et al., 2020) |
| LiMnO₂    | Spray Pyrolysis  | LiOH solution | 20 | 25°C/N | 35 | 38 | 90 | N/A | (Özgür, 2010) |
| LiMnO₂    | solid-phase      | LiCl solution | 20 | 25°C/N | 33 | 38 | 85 | N/A | (Özgür, 2010) |
| LiMnO₂    | hydrothermal     | LiCl·H₂O solution | 50 | 18°C/1 0.0 | 25 | 38 | 64 | 3.90% | (Yang et al., 2018) |
| Li₄MnO₄   | solid-phase      | Li-spiked Seawater | 30 | 16°C/7 -8 | 10 | 56 | 54 | N/A | (Hong et al., 2013) |
| Li₄MnO₄/CCTS | solid-phase   | geothermal water | 25.78 | 30°C/1 2 | 9 | 56 | 16 | 0.60% | (Wang et al., 2020) |
| Li₃TiO₃/PVC | solid-phase    | geothermal water | 25.78 | 55°C/1 2 | 12.84 | 127 | 10 | N/A | (Lin et al., 2019) |
| Li₃MnO₄   | hydrothermal     | LiCl solution | 694 | 60°C/8.0 | 39 | 44 | 90 | 0.08% | This work |

Qₜh is the theoretical adsorption capacity of sorbent, calculated based on its composition; whereas the efficiency is obtained using a measured Li⁺ uptake divided by the theoretical adsorption capacity.
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