Direct Hydrothermal Synthesis of LiMn$_2$O$_4$ Spinel and Lithium Ion Selective Adsorption

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ABSTRACT

Spinel-type ternary LiMn$_2$O$_4$ oxides precursor was synthesized via directly hydrothermal synthesis of Mn(NO$_3$)$_2$, LiOH and H$_2$O$_2$ at 383 K for 8 h. The final low-dimensional MnO$_2$ nanorod ion-sieve with lithium ion selective adsorption property was prepared further by the acid treatment process to completely extract lithium ions from the Li-Mn-O lattice. The effects of hydrothermal reaction condition on the nanostructure, chemical stability and ion-exchange property of the LiMn$_2$O$_4$ precursor and MnO$_2$ ion-sieve were systematically examined via powder X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), selected-area electron diffraction (SAED), N$_2$ adsorption-desorption and lithium ion selective adsorption measurements. The results show that this new kind of low-dimensional MnO$_2$ nanorod could be applied in lithium extraction from aqueous environment including brine, sea-water and waste water.

Keywords: LiMn$_2$O$_4$, hydrothermal synthesis, low-dimensional, ion-sieve, adsorption

1 INTRODUCTION

LiMn$_2$O$_4$ is a cubic spinel with space group symmetry Fd$ar{3}$m. The Li$^+$ is transported via 8a-16d-8a channels in the three-dimensional interstitial space provided by the [Mn$_2$O$_4$]$_2$ framework in the LiMn$_2$O$_4$ spinel with little shrinking or swelling of the spinel structure [1]. The property makes the material applicable as cathode of lithium batteries [2, 3] and selective ion-sieves for lithium adsorption from aqueous solution including brine, sea-water and waste water

2 EXPERIMENTAL

2.1 Synthesis of Low-Dimensional LiMn$_2$O$_4$ Precursor and MnO$_2$ Ion-Sieve

All chemicals used are AR reagents. 300 ml mixed solution of H$_2$O$_2$ (0.20-0.90 mol·l$^{-1}$) and LiOH (0.70-1.50 mol·l$^{-1}$) is added dropwise into a teflon-coated stainless autoclave (1000 ml) filled with 300 ml 0.40 mol·l$^{-1}$ Mn(NO$_3$)$_2$ solution stirred vigorously at 150 r·min$^{-1}$. After the mixed solution maintained in air at room temperature for 2 h, the autoclave is sealed and heated at 343-453 K for 8-48 h respectively, then cooled naturally to room temperature. The obtained black precipitate is filtrated, washed with deionized water and dried at 333 K for 8 h.

Kenta Ooi and colleagues systematically researched the Li$^+$ selective adsorption on the $\lambda$-MnO$_2$ ion-sieve [6-8]. It should be noticed that the MnO$_2$ ion-sieve obtained by conversional solid-phase reaction is of irregular morphology and large aggregate with broad particle size distribution, though improved via the optimization of the synthesis conditions [9, 10]. Rationally, the soft chemistry hydrothermal-reaction is proposed to obtain LiMn$_2$O$_4$ spinel with homogeneous composition and nanosize distribution. Kenta Ooi and colleagues [11] make LiMn$_2$O$_4$ spinel via the hydrothermal-reaction of $\gamma$-MnO$_2$ or layered compound of Li-birnessite for about 24 days or longer, yet the raw material of $\gamma$-MnO$_2$ or Li-birnessite has to be firstly prepared via a complicated process [12-14]. In the present work, a much milder hydrothermal condition is optimized to synthesize low-dimensional spinel LiMn$_2$O$_4$ precursor directly. The final low-dimensional MnO$_2$ nanorod ion-sieve with lithium ion selective adsorption property was prepared further by the acid treatment process to completely extract lithium ions from the Li-Mn-O lattice; the structure characteristics and ion-exchange properties of the samples are studied by XRD, HRTEM, SAED, N$_2$ adsorption-desorption, and lithium ion selective adsorption measurement.
\[
\text{Mn}^{2+} + \text{OH}^{-} + \text{Li}^{+} + \text{H}_2\text{O}_2 \rightarrow \text{LiMn}_2\text{O}_4 + \text{H}_2\text{O} \\
\text{Precipitation reaction:} \quad \text{Mn}^{2+} + 2 \text{OH}^{-} \rightarrow \text{Mn(OH)}_2 \\
\text{Redox reaction:} \quad \text{Mn(OH)}_2 + \text{OH}^{-} + \text{H}_2\text{O}_2 \rightarrow \text{MnOOH} + \text{H}_2\text{O} \\
\text{Li}^{+} \text{ insertion:} \quad \text{Li}^{+} + \text{MnOOH} + \text{H}_2\text{O}_2 \rightarrow \text{LiMn}_2\text{O}_4 + \text{H}_2\text{O} 
\]

### 2.2 Characterization of Samples

The bulky phase purity of the material is examined via X-ray diffraction (XRD) analysis using a Rigaku D/max 2550 X-ray diffractometer with Cu Kα radiation (\(\lambda = 1.54056 \text{ Å}\)), operating at 40 kV, 100 mA and scanning rate of 10° min⁻¹. The microstructure and surface morphology of the samples are analyzed by HRTEM and SAED on a JEOL JEM-2100F TEM (200 kV) after the samples are dispersed by ultrasonic in anhydrous ethanol for 5 min and then placed onto the cuprum grid for observations. The texture detail is characterized by N₂ adsorption-desorption at 77 K using Micromeritics ASAP 2010 V5.02, and the surface area is calculated from the Brunauer-Emmett-Teller (BET) equation, and pore volume from the total amount of nitrogen adsorbed at relative pressures of ca. 0.96 with Barrett-Joyner-Halenda (BJH) equation.

### 2.3 Lithium Ion Adsorption Measurement

The Li⁺ adsorption isotherm is carried out by stirring (150 r min⁻¹) about 100 mg ion-sieve in 100 ml LiCl solution (pH = 10.1 adjusted by buffer solution comprised of 0.1 mol⁻¹ NH₄Cl and 0.1 mol⁻¹ NH₃·H₂O, the molar ratio equal to 0.25) with different initial Li⁺ concentration for about 72 h at 303 K. The final adsorption isotherm is simulated according to Freundlich equation of

\[
\text{Q}_e = k \cdot \text{C}_e^{1/n} 
\]

The Li⁺ adsorption kinetics is carried out by stirring (150 r min⁻¹) about 100 mg ion-sieve in 100 ml LiCl solution (pH = 10.1) with uniform initial Li⁺ concentration (10.0 mmol⁻¹) at 303 K. The final adsorption kinetics is simulated according to the first order rate Lagergren equation of

\[
\ln (\text{Q}_e - \text{Q}_t) = \ln \text{Q}_e - k_\text{ads} \cdot t 
\]

The selectivity of Li⁺ compared with other coexisting cations is carried out by stirring about 100 mg ion-sieve in 10 ml mixed solution (pH = 10.1) containing Li⁺, Na⁺, K⁺, Ca²⁺ and Mg²⁺ of 10.0 mmol⁻¹ respectively for 72 h at 303 K. The concentration of all metal ions in supernatant lucid solution is determined by IC until the attainment of equilibrium. The exchange capacity or the amount of metal ion adsorbed per gram of ion-sieve at equilibrium (Qₑ), distribution coefficient (Kᵢd), separation factor (\(\alpha^{1/n}_{\text{Me}}\)) and concentration factor (CF) are calculated according to equations (5)-(8).

\[
\text{Q}_e = (\text{C}_0 - \text{C}_t) \cdot \frac{V}{W} \\
\text{Kᵢd} = \frac{(\text{C}_t - \text{C}_e) \cdot V}{(\text{C}_0 \cdot W)} \\
\alpha^{1/n}_{\text{Me}} = \frac{Kᵢd (\text{Li})}{Kᵢd (\text{Me})} \text{ Me: Li, Na, K, Ca and Mg} \\
\text{CF} = \frac{\text{Q}_e (\text{Me})}{\text{Q}_0 (\text{Me})} 
\]
shaped meso-pores with parallel walls and implies the separation of most nanorods from one another although some of the nanorods look thicker than others. Figure 2 LMO (B) is a typical HRTEM image of a single LiMn$_2$O$_4$ nanorod with inset of SAED pattern recorded on the selected area, showing reflection characteristic of one-dimensional nanorod structure, with the diffraction spots elongated in the direction perpendicular to the rod axis, and the SAED pattern also confirms that the LiMn$_2$O$_4$ ternary oxide is single crystal. The SMO ion-sieve affords the similar one-dimensional nanorod morphology with LiMn$_2$O$_4$ precursor as shown in Figure 2 SMO (A), without aggregation after the acid treatment process evidenced further by the pore size distribution curve (as shown in Figure 3) with a pore size distribution centered on 31.9 nm. Figure 2 SMO (B) is a typical HRTEM image of a single MnO$_2$ nanorod with the diameter of about 20 nm and the corresponding SAED pattern (inset) indicating that the nanorod is single crystal with the growth direction along the (111) lattice face (as shown in the arrow direction).

Figure 2: HRTEM images of LMO precursor and the SMO ion-sieve with the insets of SAED patterns respectively.

Figure 3 shows the $N_2$ adsorption-desorption isotherm of LMO precursor and SMO ion-sieve. The $N_2$ adsorption capacity of SMO ion-sieve (310 cm$^3$·g$^{-1}$, STP) is much larger than that of LMO precursor (170 cm$^3$·g$^{-1}$, STP), indicating that more meso-pores are developed after Li$^+$ extracted from the precursor. In both cases, the isotherm contains H3-type hysteresis loop with a delayed desorption branch generally occurred for capillary adsorption into interstices of compact meso-pores. The physical chemistry texture property of LMO precursor and the SMO ion-sieve are shown in Table 1. The specific surface areas ($S_{BET}$) accordingly increased from 57.85 m$^2$·g$^{-1}$ of the LiMn$_2$O$_4$ precursor to 75.75 m$^2$·g$^{-1}$ of the final MnO$_2$ ion-sieve after Li$^+$ are extracted from the Li-Mn-O lattice, contrast to the phenomena of solid-phase reaction process, in which high temperature calcinations resulted in serious aggregation of the LiMn$_2$O$_4$ and MnO$_2$ bulky particles. Pore size distribution analysis via the DFT method, applicable for a complete range of pore size indicates that both the samples afforded a mesoporous size distribution with the peak pore size ($D_p$) centered on 30.9 nm of LMO and 31.9 nm of SMO respectively. In both cases, the values of external surface area ($S_e$) and $S_{BET}$ are similar, reflecting again the lack of micropores in these samples and the very little micropore volume is also observed.

Table 1: Physical chemistry texture of LMO precursor and SMO ion-sieve

<table>
<thead>
<tr>
<th></th>
<th>$S_{BET}$ (m$^2$·g$^{-1}$)</th>
<th>$S_e$ (m$^2$·g$^{-1}$)</th>
<th>$V_T$ (cm$^3$·g$^{-1}$)</th>
<th>Hysteresis Loop</th>
<th>$D_p$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LMO</td>
<td>57.85</td>
<td>55.56</td>
<td>0.18</td>
<td>H3</td>
<td>30.9</td>
</tr>
<tr>
<td>SMO</td>
<td>75.75</td>
<td>72.94</td>
<td>0.34</td>
<td>H3</td>
<td>31.9</td>
</tr>
</tbody>
</table>

Figure 4: Li$^+$ adsorption isotherm of SMO nanorod ion-sieve and simulation according to Freundlich equation. $T = 303$ K, $pH = 10.1$, $V = 100$ ml, $W = 100$ mg.

Figure 5: Li$^+$ adsorption kinetics of SMO nanorod ion-sieve and simulation according to Lagergren equation. $T = 303$ K, $pH = 10.1$, $V = 100$ ml, $W = 100$ mg, $C_0 = 10$ mmol·l$^{-1}$. 
Figure 4 shows the Li$^+$ adsorption isotherm of the SMO nanorod ion-sieve and simulation according to Freundlich equation. The data present linearity with the congruence of $R^2 = 0.9531$, indicating that the Li$^+$ adsorption process in the experiment is accorded with the Freundlich adsorption isotherm. The adsorption constants are calculated to be $K_f = 2.26$ and $n = 14.81$. Although the value is only a little higher than that of the bulky MnO$_2$ ion-sieve (2.43 mmol·g$^{-1}$) synthesized by high-temperature calcination method [10], it is probable that the current nanorod MnO$_2$ contains trace amounts of ramsdellite-MnO$_2$ besides the cubic phase MnO$_2$ (as shown in Fig. 1) and the ramsdellite-MnO$_2$ has great defect to the Li$^+$ insertion process. Further research on the pure cubic phase nanorod MnO$_2$ synthesis is undergoing. Figure 5 shows the Li$^+$ adsorption kinetics of SMO nanorod ion-sieve and simulation according to Lagergren equation. The adsorption rate is fast till the contact time of 2 h, then the adsorption rate increases slowly and the process is close to the equilibrium. The value of the adsorption rate constant is calculated to be $K_{ads} = 6.28\times10^{-5}$ s$^{-1}$. The adsorption rate improves one order compared with bulky MnO$_2$ ion-sieve ($K_{ads} = 2.17\times10^{-6}$ s$^{-1}$) [10], indicating that the morphology and size of the ion-sieve have apparent influence on the Li$^+$ adsorption rate.

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>$Q_e$ (mmol·g$^{-1}$)</th>
<th>$K_d$ (ml·g$^{-1}$)</th>
<th>$a_{Li}^{Me}$</th>
<th>CF ($\times10^3$ l·g$^{-1}$)</th>
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<tr>
<td>Li$^+$</td>
<td>0.967</td>
<td>16770.63</td>
<td>1.00</td>
<td>95.42</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.009</td>
<td>1.07</td>
<td>15640.12</td>
<td>1.06</td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.004</td>
<td>0.46</td>
<td>36066.14</td>
<td>0.46</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.126</td>
<td>15.47</td>
<td>1084.27</td>
<td>13.32</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.230</td>
<td>32.26</td>
<td>519.80</td>
<td>24.15</td>
</tr>
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</table>

Table 2: Adsorption selectivity of Li$^+$ on SMO ion-sieve.

Table 2 shows the selectivity of Li$^+$ compared with uptake behaviors of other coexisting ions in brine including Na$^+$, K$^+$, Ca$^{2+}$, and Mg$^{2+}$. The equilibrium distribution coefficients $K_d$ are in the order of Li$^+ >>$ Ca$^{2+} >$ Mg$^{2+} >$ Na$^+ >$ K$^+$, indicating high selectivity for Li$^+$, but much less for Na$^+$, K$^+$, Ca$^{2+}$, and Mg$^{2+}$, similar to the cases of the MnO$_2$ ion-sieves prepared by solid-phase reaction, yet there exist more obvious discriminations among the values of $K_d$ and $a_{Li}^{Me}$. The distribution coefficients for Li$^+$ is $K_{d, Li} = 16770.63$ ml·g$^{-1}$, increased about 2.12 times compared with the bulky MnO$_2$ ion-sieve ($K_{d, Li} = 7917.49$ ml·g$^{-1}$) [10], indicating the remarkable improvement of the ion-sieve selectivity by the well-maintained nanorod structure. The results also indicate that Na$^+$, K$^+$, Ca$^{2+}$, and Mg$^{2+}$ in solution do not interfere with Li$^+$ during the adsorption/ion-exchange process since high concentration factor (CF) values of Li$^+$ are observed as compared with CF values of other metal ions [11].

## 4 CONCLUSION

One-dimensional spinel-type LiMn$_2$O$_4$ nanorod oxide, with the average size about 20 nm in diameter and several micrometers in length, has been directly synthesized via a simple hydrothermal synthesis of commercial Mn(NO$_3$)$_2$, LiOH and H$_2$O mixed solution at 383 K for 8 h, more favourable to control the nanocrystalline structure with well-defined pore size distribution and high surface area than traditional calcinations method, which is of great interest as an electrode material for rechargeable lithium-ion batteries. Further, the final MnO$_2$ ion-sieve with lithium ion selective adsorption capacity could be easily prepared via the acid treatment process to completely extract lithium ions from the spinel Li-Mn-O precursor, without obvious change to the Mn-O lattice structure and the one-dimensional nanorod morphology; the Li$^+$ selective adsorption behaviors of the MnO$_2$ nanorod ion-sieve are improved compared with those prepared by the conventional calcinations method, which is promising in the lithium extraction from brine or seawater.

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