Supplementary Information

Lithium adsorption performance of three-dimensional porous H₂TiO₃-type lithium ion-sieve in strong alkaline Bayer liquor

Xin Xu, ^{a,b,c} You Zhou, ^{a,b} Maohong Fan,^c Zijian Lv,^a Yang Tang, ^{a,b} Yanzhi Sun, ^{a,b} Yongmei Chen, ^{a,b,*} and Pingyu Wan ^{a,b}

^a National Fundamental Research Laboratory of New Hazardous Chemicals Assessment & Accident Analysis, Beijing University of Chemical Technology, 100029 Beijing, P. R. China

^b Institute of Applied Electrochemistry, Beijing University of Chemical Technology, 100029 Beijing, P. R. China

^c Department of Chemical and Petroleum Engineering, University of Wyoming, Laramie, WY 82071, USA

Corresponding author: Yongmei Chen Address: Beijing University of Chemical Technology, Chaoyang District, No.15, North 3rd Ring Road East, Beijing, P. R. China Email: <u>chenym@mail.buct.edu.cn</u> Telephone: 0086-13683294397

Notes

The authors declare no competing financial interest.



Figure S1. XPS image of full spectra for porous-LTO, porous-HTO, and Li⁺-loaded porous-HTO.



Figure S2. 3D ordered self-assembly colloidal PS microspheres in different magnifications.

The 3D ordered self-assembly colloidal PS microspheres present highly homogeneous and close-packed structure, which ensure uniform in pore size of porous Li_2TiO_3 and H_2TiO_3 . The sizes of PS microspheres are narrowly distributed and the average diameter is *ca.* 174 nm. As a matter of fact, the interaction connection force between PS microspheres is very weak; usually it could be easily destroyed by the water molecular acting force. Thus, the precursor solution could fully permeate into the interstitial space of the PS colloidal.



Figure S3. Pseudo-first-order kinetic fitting curves of (a) bare-HTO, (c) porous-HTO; pseudo-second-order kinetic fitting curves of (b) bare-HTO, (d) porous-HTO in the simulation Bayer liquor at room temperature.



Figure S4. (1) XRD patterns of (a) Mn-LIS precursor, (b) Mn-LIS, and (c) Li-loaded Mn-LIS in Li⁺containing alkaline solution (6.0 mol·L⁻¹ NaOH, 56.00 mg·L⁻¹ Li⁺); (2) Equilibrium lithium adsorption capacity changes of Mn-LIS in 5 cycle operation in Li⁺-containing alkaline solution (6.0 mol·L⁻¹ NaOH, 56.00 mg·L⁻¹ Li⁺), and (3) comparison of Mn dissolution ratios in 5 cycle operation (in both 6.0 mol·L⁻¹ and 0.01 mol·L⁻¹ OH⁻ solution).

Figure S4(1) shows the structural change of Mn-LIS before and after loading lithium in strong alkaline solution. Figure S4(1a) shows the diffraction peaks at $2\theta = 18.642^{\circ}$, 36.156° , 37.817° , 43.903° , 48.203° , 58.778° , 63.506° which could be readily indexed to LiMn₂O₄ (*Fd-3m* space group, JCPDS card 35-0782), indicating the precursor of Mn-LIS present typical spinel structure, cubic phase.[1] Figure S4(1b) shows Mn-LIS exhibits the same spinel structure as the precursor, implying λ -MnO₂ spinels keep their molecular framework in de-lithiation process. However, the XRD pattern of Mn-LIS changes dramatically after loading lithium from the strong alkali solution as shown in Figure S4(1c). It is observed that

although the main peak of spinel phase (111) could be detected, lots of peaks that derived from impurities such as Mn_2O_3 , Mn_2O_3 , MnO_2 and $Mn(OH)_2$ also appear. This implies the spinel λ -MnO₂ structure has probably been collapsed to a certain extend in the strong alkaline solution. In comparison, the reported studies showed that the Li-loading Mn-LIS from salt-lake brines/sea water usually presented better reproducibility, that is, the XRD patterns of Mn-LIS before and after loading lithium were quite similar and no impurities were detected.[2, 3] The XRD patterns give a direct evidence of structural changes of Mn-LIS before/after loading Li⁺ ions from strong alkaline aqueous solution.

Figure S4(2) illustrates the changes in the equilibrium lithium adsorption capacity of Mn-LIS with increasing cycle times. For the first cycle, the average lithium uptake capacity is about 14.40 mg·g⁻¹, which is only about 36 % of the theoretical lithium adsorption value $(40.00 \text{ mg} \cdot \text{g}^{-1})$ of the Mn-LIS. However, previous studies revealed that the practical lithium equilibrium adsorption capacity could reach 23.73 mg·g⁻¹ (about 62.1 % of the theoretical lithium adsorption value) in the environment of pH=12.17.[1] This indicates that the adsorbent activity in strong alkali solution drops significantly as compared with in the reported optimized condition. In addition, a large deviation exists in the repeated determination of the first cycle (between 10.71 mg·g⁻¹ and 18.12 mg·g⁻¹), implying the structure of Mn-LIS is unstable in strong alkaline medium. Even worse, the lithium uptake decreases to 4.20 mg·g⁻¹ sharply at the second cycle and then kept at a very low level of 2.56 mg \cdot g⁻¹ in the following cycles. The Mn dissolution ratios of Mn-LIS in 6.0 mol·L⁻¹ to 0.01 mol·L⁻¹ alkaline solution after 5 cycle operation are compared in Figure S4(3). The results show that the average manganese loss in Mn-LIS is more than 9 % in strong alkaline solution while only less than 1.5 % in weak alkaline solution, suggesting the lithium adsorption activity of the adsorbent has lost after 5 cycles' regeneration, and the structure of Mn-LIS might be changed dramatically in the strong alkaline medium.

[2] Q.-H. Zhang, S. Sun, S. Li, H. Jiang, J.-G. Yu, Adsorption of lithium ions on novel nanocrystal MnO₂,

^[1] Q.H. Zhang, S.P. Li, S.Y. Sun, X.S. Yin, J.G. Yu, LiMn₂O₄ spinel direct synthesis and lithium ion selective adsorption, Chemical Engineering Science, 65 (2010) 169-173.

Chemical Engineering Science, 62 (2007) 4869-4874.

[3] S.-Y. Sun, J.-L. Xiao, J. Wang, X. Song, J.-G. Yu, Synthesis and Adsorption Properties of $Li_{1.6}Mn_{1.6}O_4$ by a Combination of Redox Precipitation and Solid-Phase Reaction, Industrial & Engineering Chemistry Research, 53 (2014) 15517-15521.

Adsorbents	Ions	$C_{\theta} (\mathrm{mg}\cdot\mathrm{L}^{-1})$	$C_e (\mathrm{mg}\cdot\mathrm{L}^{-1})$	$Q_e (\mathrm{mg}\cdot\mathrm{g}^{-1})$	$K_d (\mathrm{mL} \cdot \mathrm{g}^{-1})$	$lpha_{\scriptscriptstyle M\!e}^{\scriptscriptstyle Li}$	$CF(L \cdot mg^{-1})$
Bare-HTO	Li ⁺	60.04	19.54	40.50	2072.67	1.00	674.55
	Na ⁺	60.13	59.16	0.97	16.40	126.41	16.13
Porous-HTO	Li ⁺	60.04	6.37	53.67	8425.43	1.00	893.90
	Na ⁺	60.13	59.48	0.65	10.93	770.99	10.81

Table S1. The comparison between Lithium and sodium adsorption by both bare-HTO and porous-HTO in the simulation Bayer liquor