

Article

Synthesis of Porous Lithium Ion Sieve with High Purity for Li^+ Adsorption

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Abstract: With the depletion of solid lithium ore, extracting lithium from salt lake brine has become a critical focus for future endeavors. A four-step method was used to synthesize high-purity $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ for extracting Li^+ . Porous cubic Mn_2O_3 was hydrothermally synthesized with carbon spheres and surfactants as templates. Then, it was converted to LiMnO_2 by calcining with Li_2CO_3 . After roasting and acid pickling, $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ was successfully synthesized. The impacts of calcination temperature, Li/Mn molar ratio and glucose addition on LiMnO_2 composition, loss percentage of dissolved Mn in precursor, and the adsorption characteristics of the lithium ion sieve were studied. Glucose inhibited the formation of LiMn_2O_4 and promoted the formation of pure LiMnO_2 . The resulting precursor without impurities showed porous structure. After acid pickling, $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ showed a high-adsorption performance and excellent cycle performance. After five cycles, adsorption capacity remained above 30 mg/g, and the loss percentage of dissolved Mn stabilized at about 1%. The Li^+-H^+ exchange conformed to pseudo-second-order adsorption dynamics and the Langmuir adsorption isotherm equation, indicating that the adsorption process can be classified as monolayer chemical adsorption.

Keywords: lithium ion sieve; solid-phase synthesis; adsorption capacity

1. Introduction

As lithium battery and new energy industries experience rapid growth [1–4], the demand for lithium in China and the world has soared [5–8]. The lithium resource in China is generally categorized into solid lithium ore and liquid brine [9–11]. Notably, approximately 80% of the total lithium reserve is found in salt lakes [12–14]. Due to the exhaustion of solid lithium ore, the extraction and recovery of lithium from salt lake brine has attracted significant attention. At present, several methods are used to separate and extract lithium, including membrane separation [15,16], solvent extraction [17–19], and adsorption methods [20–22]. Among these, the adsorption method stands out as an ideal and prospective approach due to its excellent separation effect, environmental sustainability, and economic advantages [14]. Compared with other adsorbents, the Mn-based adsorbent has high selectivity for lithium and superior adsorption properties. It typically includes various kinds of lithium ion sieves, such as HMn_2O_4 [23], $\text{H}_4\text{Mn}_5\text{O}_{12}$ [24], and $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ [25,26]. $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ is synthesized by roasting LiMnO_2 to obtain the precursor $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ and then replacing Li^+ with H^+ , resulting in the ion exchange to adsorb Li^+ and exhibiting the maximum lithium adsorption capacity. Chitrakar [27] developed and utilized a $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ adsorbent for recovering lithium from seawater in the initial stages. Hayashi [28] synthesized a $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ rod with an adsorption capacity of 5.6 mmol g^{-1} . And researchers have also explored the Li^+ extraction mechanism [29–31].



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However, the composition of LiMnO_2 and the morphology of $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ have great effect on the performance of $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ [25]. The presence of a small amount of Mn^{3+} in the precursor could lead to an unstable spinel structure and deterioration in cycling performance due to disproportionation during acid pickling [32].

Adsorbents characterized by numerous different pores structures promote effective adsorption because they expose additional adsorption sites for ion exchange [33]. And the distribution of appropriate pore sizes can effectively reduce the diffusion pathway for Li^+ , thereby enhancing the overall adsorption performance. Simultaneously, the Mn-based lithium ion sieve with porous structure has a relatively large specific surface area, which is conducive to facilitating Li^+ migration and improving the adsorption rate [34,35]. Xu [36] synthesized a lithium ion sieve using attapulgite with a large surface area, which provided an adsorption capacity of 29.18 mg/g. Finally, porous structures feature a large gas channel, which is beneficial to oxygen diffusion and provides thorough contact with the bulk of crystal LiMnO_2 . As a result, LiMnO_2 can be completely oxidized to obtain high-purity $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ with traces of Mn^{3+} [23,25].

In this study, porous Mn_2O_3 was firstly synthesized by template method. Then, Mn_2O_3 , Li_2CO_3 , and glucose were calcined by carbothermal reduction-assisted solid-phase method [37] to obtain pure LiMnO_2 . Finally, LiMnO_2 was converted to the precursor through roasting, and then, the lithium ion sieve was synthesized after acid pickling.

2. Materials and Methods

2.1. Materials

The reagents $\text{C}_6\text{H}_{12}\text{O}_6$, Li_2CO_3 , HCl , and $\text{C}_2\text{H}_5\text{OH}$ were from Sinopharm Group Chemical Reagent Co., Ltd. (Shanghai, China). The reagents $\text{Mn}(\text{CH}_3\text{COO})_2$, polyvinylpyrrolidone (PVP), and $\text{CO}(\text{NH}_2)_2$ were supplied by Aladdin Industrial Co., Ltd. (Shanghai, China). These were all AR reagents. The salt lake brine was from Lop Nor Lake in the Xinjiang Uygur Autonomous Region of China.

2.2. Methods

2.2.1. Synthesis of Porous Cubic Mn_2O_3

Firstly, carbon sphere [38] was prepared by hydrothermal treatment of 1 mol/L glucose solution at 200 °C for 24 h. The porous Mn_2O_3 was synthesized according to the method of Shao Y [39]. Urea $\text{CO}(\text{NH}_2)_2$ as precipitant and $\text{Mn}(\text{CH}_3\text{COO})_2$ as manganese salt were used to hydrothermally synthesize MnCO_3/C composites with carbon spheres and surfactant PVP (PVP is a nonionic polymer compound) as templates. Next, 2 g carbon spheres and 10 g PVP were dispersed into water and stirred for 12 h. Then, $\text{CO}(\text{NH}_2)_2$ and $\text{Mn}(\text{CH}_3\text{COO})_2$ were added according to a molar ratio of manganese salt to precipitant of 1:40. After vigorous stirring, the suspension was transferred to an autoclave and hydrothermally reacted at 90 °C for 12 h. MnCO_3/C composites were obtained after filtering, washing, and drying. Finally, MnCO_3/C was transformed into porous Mn_2O_3 by calcining at 600 °C for 6 h in a muffle furnace [34].

2.2.2. Synthesis of LiMnO_2 and Precursor $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$

Li_2CO_3 , porous Mn_2O_3 , 5% (equivalent to the mass of Mn_2O_3) of glucose, and an appropriate amount of anhydrous ethanol were thoroughly ground to fully and evenly mix them. Then, the mixture was calcined in a closed tube furnace with nitrogen blowing at 750 °C for 6 h to obtain LiMnO_2 . Finally, LiMnO_2 was roasted at 450 °C for 6 h to synthesize the precursor $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ [40].

2.2.3. Synthesis of Lithium Ion Sieve

A small quantity of $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ was added to 0.5 mol/L hydrochloric acid solution. The Mn-based lithium ion sieve was successfully synthesized after acid pickling at 30 °C for 4 h.

2.2.4. Adsorption and Cycling Performance

The lithium ion sieve was put into a certain volume of brine and stirred to facilitate Li^+ adsorption. Adsorption capacity (Q) was calculated by following Equation (1):

$$Q = \frac{V(C_0 - C_1)}{m}, \quad (1)$$

where Q represents the Li^+ adsorption capacity of $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ ($\text{mg} \cdot \text{g}^{-1}$); C_0 and C_1 represent the concentration of Li^+ in solution before adsorption and after adsorption, respectively ($\text{mg} \cdot \text{L}^{-1}$); V represents the volume of salt lake brine (L); m represents the mass of $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ (g).

The loss percentage of dissolved Mn (R_{Mn}) in acid pickling was calculated by Equation (2):

$$R_{\text{Mn}} = \frac{C_{\text{Mn}}V}{m_s W}, \quad (2)$$

where R_{Mn} represents the loss percentage of dissolved Mn (%); C_{Mn} represents the concentration of Mn^{2+} in filtrate after acid pickling ($\text{mg} \cdot \text{L}^{-1}$); V represents the volume of hydrochloric acid (L); m_s represents the mass of the precursor (g); W represents the mass fraction of Mn in the precursor (%).

The acid pickling and adsorption of Li^+ were repeated for several times, and then, the cycling performance was determined. In each acid pickling process, the precursor $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ was put into 0.5 mol/L hydrochloric acid solution for delithiation. After filtering, washing, and drying, $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ was transferred into salt lake brine at 30 °C for 24 h to adsorb Li^+ . These above operations were considered as one complete cycle. After this process, the concentrations of Mn and Li were measured to calculate the loss percentage of dissolved Mn and adsorption capacity in every cycle using Equation (1) and Equation (2), respectively.

2.2.5. Evaluation of Adsorption Selectivity

The adsorption selectivity of $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ is a crucial indicator under competitive conditions, particularly in the presence of co-existing ions such as Na^+ and Mg^{2+} . A small amount of $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ was put into brine for adsorption. Subsequently, the concentrations of metal ions were measured to calculate the adsorption capacity and distribution coefficient (K_d) as follows:

$$K_d = \frac{(C_0 - C_1)V}{mC_1}, \quad (3)$$

where K_d represents the distribution coefficient of different ions ($\text{mL} \cdot \text{g}^{-1}$); C_0 and C_1 represent the concentration of ions in solution before adsorption and after adsorption, respectively ($\text{mg} \cdot \text{L}^{-1}$); V represents the volume of salt lake brine (L); m represents the mass of $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ (g);

2.2.6. Evaluation of Adsorption Kinetics

A small amount of $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ was put into brine at room temperature for certain time and sampled at regular interval to measure the concentration of Li^+ for calculating adsorption capacity. The H^+ – Li^+ exchange process was simulated using pseudo-first-order and pseudo-second-order dynamics models and the intraparticle diffusion model, respectively.

The equations of three adsorption kinetics are as follows:

$$\lg(Q_e - Q_t) = \lg Q_e - \frac{t \cdot k_1}{2.303}, \quad (4)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 \cdot Q_e^2} + \frac{1}{Q_e} t, \quad (5)$$

$$\text{and } Q_t = K_i \cdot t^{0.5} + C \quad (6)$$

where Q_t represents the adsorption capacity of $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ at given time ($\text{mg} \cdot \text{g}^{-1}$); Q_e represents the adsorption capacity of $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ at equilibrium ($\text{mg} \cdot \text{g}^{-1}$); t represents adsorption time (h); k_1 , k_2 , and K_i represent the adsorption kinetic rates, respectively; C is the intercept.

2.2.7. Determination of Adsorption Isotherm

A small amount of $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ was put into LiCl solutions with different concentrations at room temperature for 24 h to adsorb Li^+ . The adsorption isotherm was simulated using Langmuir and Freundlich models, respectively.

The equations of the two models are as follows:

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \quad (7)$$

$$\text{and } \lg Q_e = \frac{1}{n} \lg C_e + \lg K_F, \quad (8)$$

where C_e represents the Li^+ equilibrium concentration ($\text{mg} \cdot \text{L}^{-1}$); Q_e represents the adsorption capacity of $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ at equilibrium ($\text{mg} \cdot \text{g}^{-1}$); Q_m represents the theoretical maximum adsorption capacity of $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ ($\text{mg} \cdot \text{g}^{-1}$); K_L and K_F represent the adsorption isothermal constants, respectively.

2.2.8. Analysis and Characterization

The concentrations of ions were quantified after acid pickling and adsorption using inductively coupled plasma spectrometer (ICP, Thermo Fisher Scientific, Waltham, MA, USA). Phase composition was analyzed using X-ray diffractometer (XRD, PANalytical B.V., Almelo, The Netherlands). The morphology of the precursor was characterized using scanning electron microscope (SEM, JEOL, Tokyo, Japan).

3. Results

3.1. Properties of Porous Mn_2O_3

XRD patterns of MnCO_3/C and Mn_2O_3 are presented in Figure 1. Its diffraction peak is very sharp in Figure 1a, which is consistent with MnCO_3 (PDF NO. 44-1472). There are no carbon and other impurity diffraction peaks. This indicates the synthesized MnCO_3 has good crystallinity and purity. The calcined Mn_2O_3 also shows sharp peaks identified with cubic $\alpha\text{-Mn}_2\text{O}_3$ (PDF NO. 24-0508), meaning that it is highly crystalline and pure.

Figure 2 illustrates the morphologies of carbon spheres and cubic Mn_2O_3 . According to the SEM image presented in Figure 2a, it can be observed that carbon spheres are intact and have uniform size ranging from 800 nm to 1.5 μm . From Figure 2b, Mn_2O_3 maintains a complete cubic shape with size around 6–8 μm . However, there are numerous spherical concaves on the particle surface, and the dimensions of these concaves are similar to those of carbon spheres. It can be inferred that these concaves were formed during the calcining process of carbon spheres. Additionally, as shown in the partially enlarged image (Figure 2c), the Mn_2O_3 cubic structure has some interconnected channels with a width of more than 20 nm. These channels may result from both the decomposition of MnCO_3 and the oxidation of carbon spheres during calcination [41]. The release of CO_2 contributes to the channel formation. Furthermore, PVP as a soft template also releases CO_2 during this process [42], leading to the formation of more gaps on the surface of the Mn_2O_3 cubic structure.

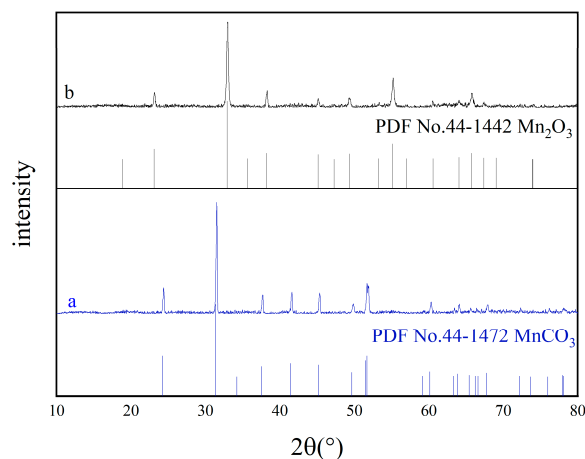


Figure 1. XRD patterns of (a) MnCO_3/C and (b) Mn_2O_3 .

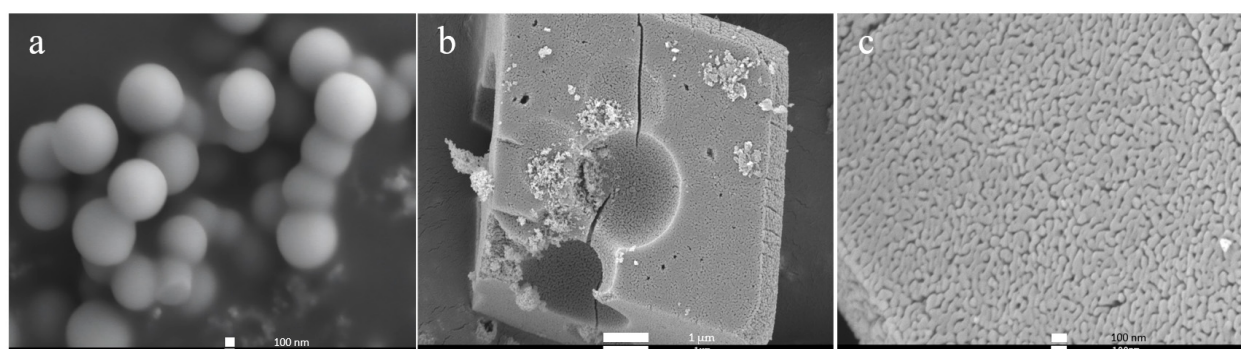


Figure 2. SEM images of (a) carbon spheres, (b) cubic Mn_2O_3 , (c) and the partial enlargement.

3.2. Synthesis of LiMnO_2

3.2.1. Optimization of Calcination Temperature

Figure 3 presents XRD patterns of samples obtained at various calcination temperatures. As shown, a pure phase of LiMnO_2 was obtained at 650 °C and 750 °C. However, only a small amount of LiMnO_2 was produced at 550 °C, with the majority being LiMn_2O_4 . The diffraction peaks of LiMnO_2 are weak, and crystallization is incomplete at 550 °C. The intensity and purity of diffraction peaks also increases when the calcination temperature rises, facilitating the formation of a pure product. At a temperature of 850 °C, a small amount of Mn_3O_4 impurity appears, which results from the decomposition of Mn_2O_3 .

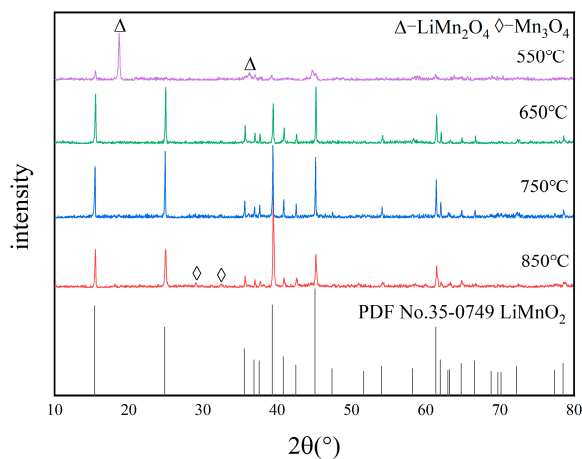


Figure 3. XRD patterns of samples at different calcination temperatures.

3.2.2. Optimization of Molar Ratio of Lithium to Manganese

Figure 4 illustrates the XRD patterns of samples synthesized at various molar ratios of lithium to manganese (Li/Mn). It can be observed from Figure 4 that pure LiMnO_2 can be successfully obtained no matter what the Li/Mn ratio is. But as the Li/Mn ratio reaches 1.03, the resulting diffraction peaks are sharper compared to those with other ratios, and the crystallization is also more complete. When the Li/Mn ratio is 1.05 and 1.08, the intensity of the LiMnO_2 diffraction peak is weaker compared to that observed at a Li/Mn ratio of 1.03. An excessive Li/Mn ratio results in a large amount of Li^+ entering into the structure, even affecting the transition element layer [32]. This impacts the structural integrity of LiMnO_2 , resulting in poor crystallinity and a mixing phenomenon of cations within the precursor [43]. From an economic perspective, a Li/Mn ratio of 1.03 represents an optimal choice.

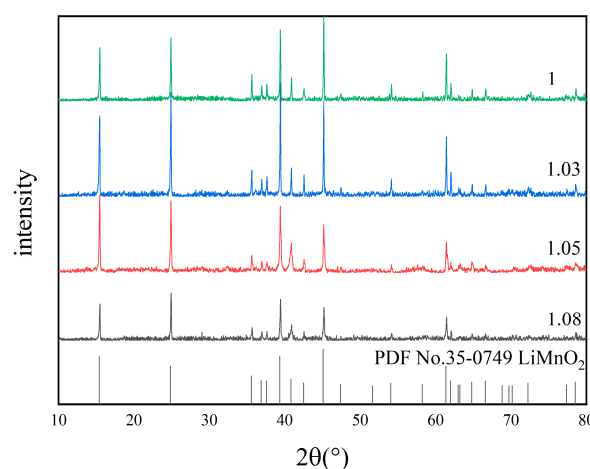
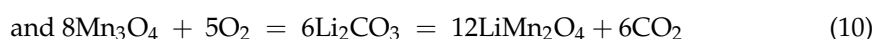


Figure 4. XRD patterns of samples with different Li/Mn ratios.

3.2.3. Optimization of Glucose Content

Figure 5 presents the XRD patterns of LiMnO_2 synthesized with various amount of glucose (relative to Mn). As shown in Figure 5, the intensity of impurity peaks is weaker, and the LiMnO_2 main peak becomes sharper with the increase in glucose content. LiMn_2O_4 impurity peaks are observed for the blank and 3% glucose. In contrast, pure LiMnO_2 can be obtained when the glucose content exceeds 5%. Glucose does not affect the composition of subsequent products. The presence of LiMn_2O_4 impurity primarily arises from the decomposition of a portion of Mn_2O_3 during the high-temperature synthesis process of LiMnO_2 , leading to small quantities of Mn_3O_4 and O_2 [37]. This part of Mn_3O_4 and O_2 subsequently reacts with lithium to form LiMn_2O_4 . Simultaneity, excess O_2 when glucose is insufficient may also oxidize a minor amount of LiMnO_2 into LiMn_2O_4 . The relevant chemical equations are shown in (9) and (10):



In the high-temperature solid-phase reaction process, the decomposition of Mn_2O_3 is unavoidable. Therefore, altering process parameters, such as the calcination temperature or the molar ratio of Li/Mn, does not completely eliminate the impurity of LiMn_2O_4 . Impurities in LiMnO_2 can lead to impure composition during the synthesis of the precursor $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$. This adversely affects the structure and purity of the lithium ion sieve, resulting in a decreased adsorption capacity and an increased Mn dissolution loss percentage. Although HMn_2O_4 has a certain adsorption capacity, its adsorption properties are inferior

to those of $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$. Therefore, the presence of impurities in LiMnO_2 may result in an unsatisfactory adsorption performance of the subsequently formed lithium ion sieve. Yu [44] also confirmed the view by analyzing the obvious positive correlation between the adsorption density of Li and the content of $\text{H}_4\text{Mn}_5\text{O}_{12}$. So, the addition of glucose is essential. Firstly, glucose can directly consume O_2 within the reaction environment, thereby protecting LiMnO_2 from oxidation. Secondly, glucose can reduce partial impurities back into LiMnO_2 . Thus, two functions synergistically contribute to synthesizing pure LiMnO_2 . Glucose acts as a reducing agent to protect LiMnO_2 from oxidation and does not remain within the adsorbent after synthesis. Consequently, high-purity LiMnO_2 can be synthesized through carbothermal reduction-assisted solid-phase reactions.

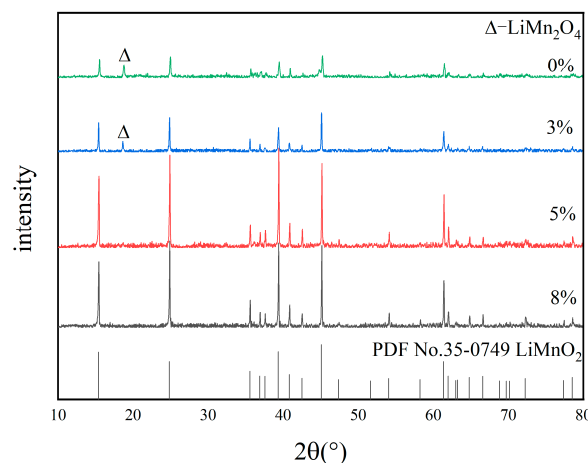


Figure 5. XRD patterns of samples with different glucose amounts.

3.3. Characterization of $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$

According to the above results, the optimal synthetic conditions are as follows: calcination temperature of $750\text{ }^\circ\text{C}$, molar ratio of Li/Mn of 1.03, and addition of glucose at 5%. $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ can be obtained by roasting LiMnO_2 at $450\text{ }^\circ\text{C}$ for 6 h. Figure 6 illustrates the SEM image and XRD pattern of $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$. As shown in Figure 6a, the particles of $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ aggregate into cubic structures with obvious gaps. Some gaps conjunct together and even form holes. The features may facilitate the formation of suitable channels that allow for the free movement of Li^+ in and out without destroying the spinel structure [45]. The structural framework closely resembles cubic Mn_2O_3 (Figure 2b). Furthermore, as presented in Figure 6b, the diffraction peak is consistent with $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ (PDF NO.52-1841), indicating that the product is composed of $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ monophase with cubic crystal structure.

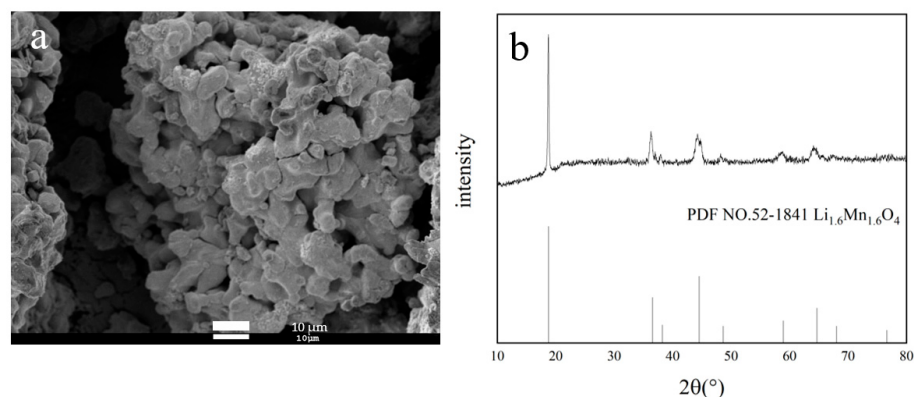


Figure 6. (a) SEM image and (b) XRD pattern of $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$.

4. Discussion

4.1. Adsorption Performance of $H_{1.6}Mn_{1.6}O_4$

Figure 7 shows the loss percentage of dissolved Mn of the precursor by roasting $LiMnO_2$ and the adsorption capacity for Li^+ at various calcination temperatures, molar ratios of Li/Mn, and glucose contents. In Figure 7a, $H_{1.6}Mn_{1.6}O_4$ shows a maximum adsorption performance of about 34.7 mg/g and a minimum Mn dissolution loss of about 3.4% at 750 °C. The change of the Mn dissolution loss percentage with calcination temperature is due to the fact that a low calcination temperature leads to $LiMn_2O_4$ formation and a high temperature to Mn_3O_4 , as shown in Figure 3. Those two species contain Mn^{3+} and cause a disproportionation reaction in hydrochloric acid, resulting in the formation of Mn^{4+} and Mn^{2+} . The release of Mn^{2+} into solution leads to a relatively high percentage of Mn dissolution loss. Figure 7b shows the Li/Mn ratio has a small effect on the adsorption performance and loss percentage of dissolved Mn, and this response is consistent with the result in Figure 4. However, the adsorption performance and loss percentage of dissolved Mn have great dependence on the glucose content. When it is less than 5%, a high glucose content is beneficial for improving the adsorption capacity and structure stability, as shown in Figure 7c. Further increasing the glucose content has no obvious effect compared with 5% glucose. At same time, it can be observed that the lithium ion sieve obtained by roasting $LiMnO_2$ without impurities and acid pickling has a higher adsorption capacity and lower loss percentage of dissolved Mn than that obtained by roasting $LiMnO_2$ containing impurities and acid pickling. These results indicate that the composition of $LiMnO_2$ has a great difference from the performance of the Mn-based lithium ion sieve [25].

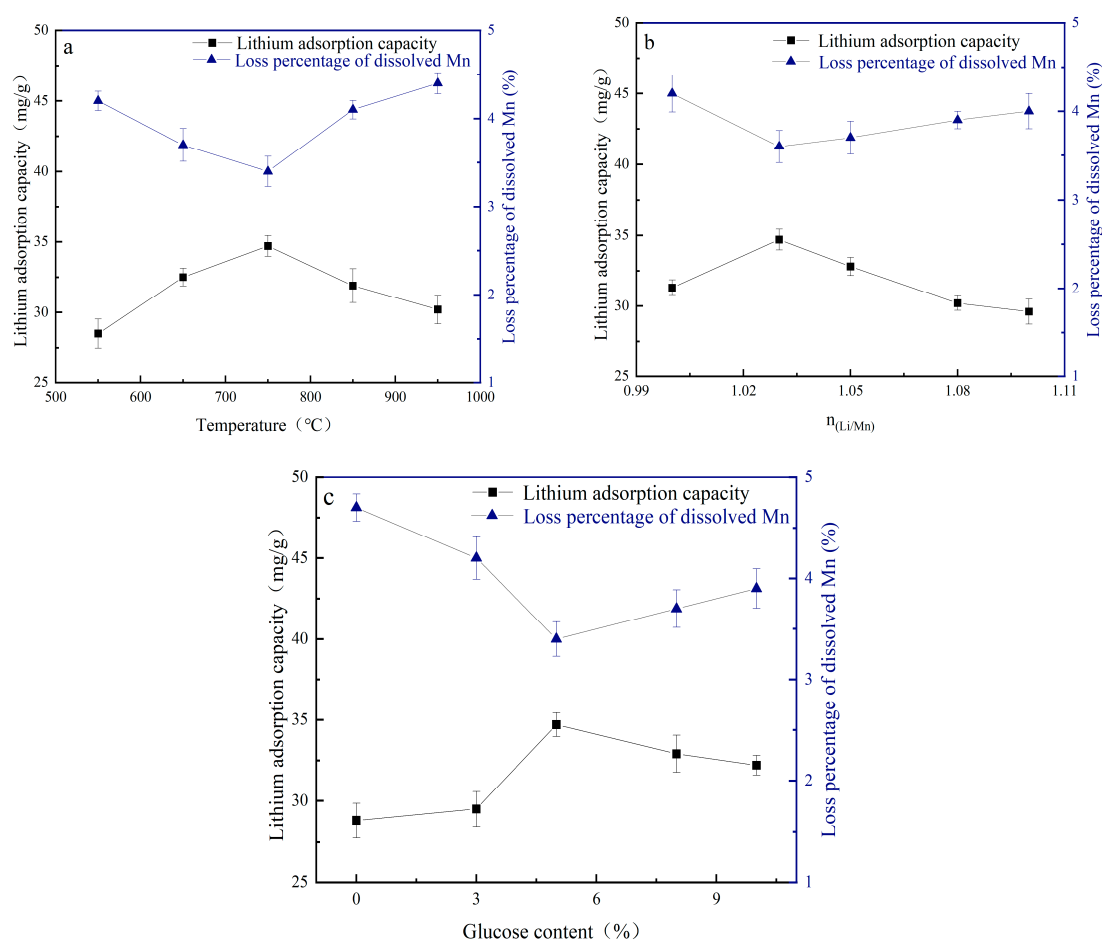


Figure 7. The loss percentage of dissolved Mn and corresponding adsorption capacity at different (a) calcination temperatures, (b) molar ratios of Li/Mn, and (c) glucose contents.

Table 1 describes the performance of other solid-phase synthetic non-porous lithium ion sieves. Compared to the references, the Li^+ adsorption capacity is improved. This enhancement can be attributed to the porous cubic structure of $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ particles. A porous structure is conducive to Li^+ migration and exchange, leading to a higher adsorption capacity [46]. Li [47] also confirmed the view by synthesizing 3D macroporous–mesoporous $\text{H}_4\text{Ti}_5\text{O}_{12}$ and porous $\text{H}_4\text{Ti}_5\text{O}_{12}$. They found higher Li^+ adsorption capacity compared with nonporous $\text{H}_4\text{Ti}_5\text{O}_{12}$ because of the highly interconnected porous channel.

Table 1. Performance of other solid-phase synthetic non-porous lithium ion sieves.

Precursor	Adsorption Capacity (mg/g)	Loss Percentage of Dissolved Mn (%)	Cite
LiMn_2O_4	30.9	25	[48]
LiMn_2O_4	32.8	-	[49]
$\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$	29.4	1.62	[50]
$\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$	34.7	3.4	This article

4.2. Cycling Performance

The loss percentage of dissolved Mn during acid pickling and Li^+ adsorption capacity were determined over multiple cycles. The results are illustrated in Figure 8. During the initial three cycles, the loss of dissolved Mn is due to the Mn^{3+} disproportionation reaction in hydrochloric acid [51]. After three cycles, nearly all Mn^{3+} was dissolved, and the percentage of Mn dissolution loss presented a constant value approximately 1%. This stability can be attributed to the formation of high-purity precursor $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ following the roasting of LiMnO_2 without impurities. Figure 8 also demonstrates that the lithium adsorption capacity decreases as the number of cycles increases. This reduction can be attributed to the H^+ – Li^+ ion exchange process during the acid pickling, where H^+ possesses smaller ionic radius compared to Li^+ [52]. During the adsorption process, this exchange between Li^+ and H^+ inevitably leads to a contraction of the crystal structure. Consequently, this phenomenon hinders both diffusion and embedding of Li^+ into the crystal lattice, ultimately leading to a decreased lithium adsorption capacity. After five cycles, the adsorption capacity remained more than 30 mg/g, and recovery rate was about 85%. The resulting lithium ion sieve therefore exhibits high stability during cycling.

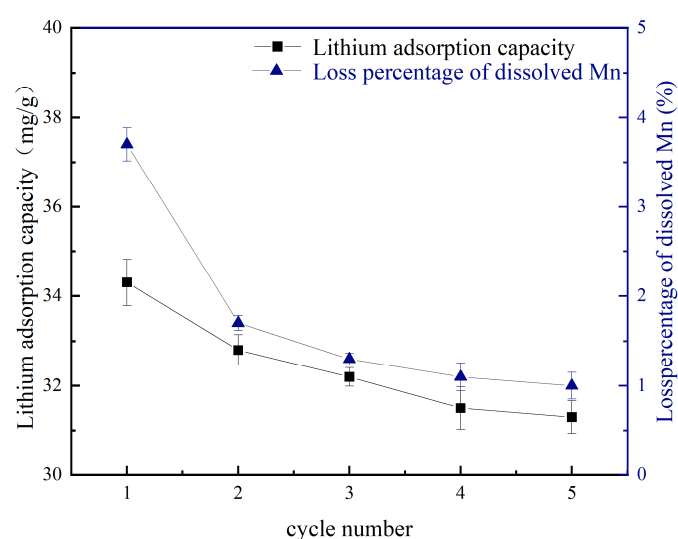


Figure 8. Loss percentage of dissolved Mn and corresponding adsorption capacity of precursors during circulation.

4.3. Adsorption Selectivity

The existence of various ions in salt lake brine has a significant impact on the Li^+ adsorption effect of the lithium ion sieve. Figure 9 demonstrates the adsorption capacity of $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ for Li^+ , Mg^{2+} , K^+ , and Na^+ . $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ has the highest adsorption capacity for Li^+ compared to Mg^{2+} , K^+ , and Na^+ , and the distribution coefficient of Li^+ is much larger than that of other ions. These results indicate the synthesized lithium ion sieve exhibits exceptional selectivity for Li^+ .

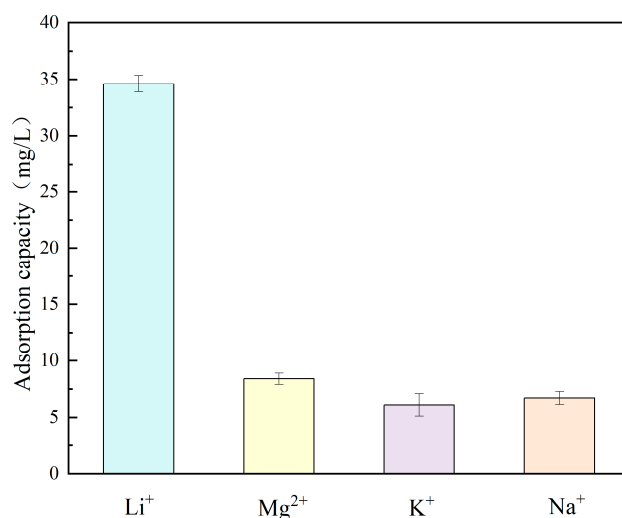


Figure 9. Adsorption capacity for various ions.

4.4. Adsorption Kinetics

The variation in adsorption capacity over time is illustrated in Figure 10. As shown, adsorption capacity progressively enhances over time. The initial adsorption rate is notably rapid during the first stage but subsequently slows down. This is due to the fact that there are numerous lithium vacancies exhibiting a memory effect within the spinel structure after acid pickling. Additionally, a significant concentration gradient of Li^+ between brine and the interior of ion sieve is beneficial for Li^+ to enter into the crystal lattice and cause exchange with H^+ [53]. However, H^+ in $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ enters into the solution as time goes by, leading to an increase in the concentration of H^+ . Simultaneously, as Li^+ is adsorbed into the ion sieve, there is a decline in the Li^+ concentration in brine. These factors hinder both the Li^+ – H^+ exchange and overall adsorption processes. Thus, the initial rate of adsorption is fast, while the subsequent adsorption rate gradually becomes gentle.

Figure 11 illustrates three kinetic models for adsorption process of lithium ion sieve. Using the pseudo-first-order adsorption dynamics model gives a linear correlation coefficient of about only 0.912. However, the linear correlation coefficient increases significantly to 0.999, and the adsorption constant K is 0.051 based on the pseudo-second-order adsorption dynamics model. Figure 11c shows that the resulting straight lines do not pass through the origin, and the correlation coefficients are lower than that of the pseudo-second-order kinetic model. These results show the process of ion exchange between Li^+ and H^+ is not consistent with the pseudo-first-order dynamics model and intraparticle diffusion model but closely conforms to the pseudo-second-order adsorption dynamics model. These findings suggest the adsorption process of the lithium ion sieve is primarily controlled by chemical adsorption.

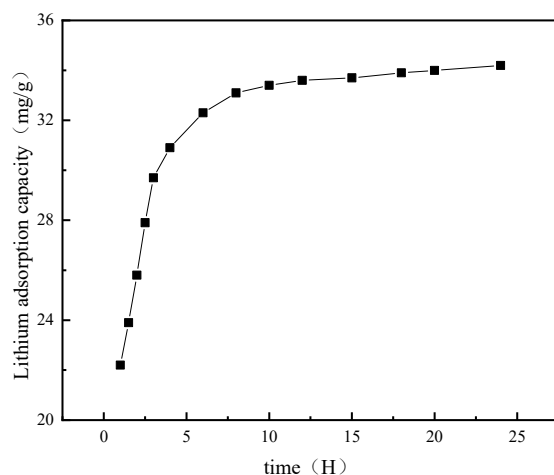


Figure 10. The variation in adsorption capacity over time.

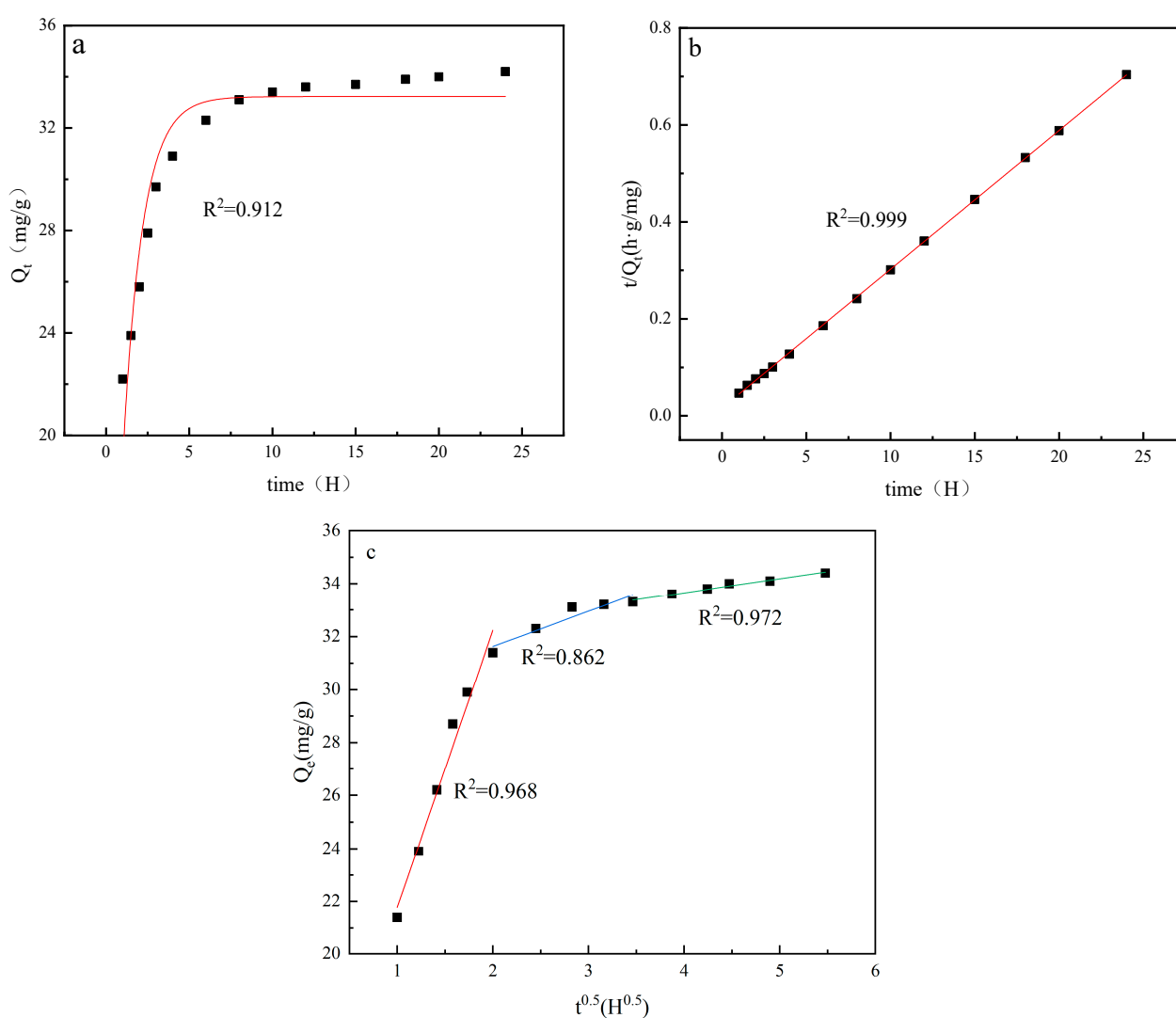


Figure 11. Fitting results of (a) pseudo-first-order dynamics, (b) pseudo-second-order dynamics, and (c) intraparticle diffusion model.

4.5. Adsorption Isotherm

Figure 12 presents the adsorption isotherm of the lithium ion sieve and the fitting results with Langmuir and Freundlich models. With the increase in Li^+ concentration in

the solution, the adsorption capacity of $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ also correspondingly increases. The correlation coefficient based on the Langmuir equation is 0.999, while that of the Freundlich model is just 0.927. The results indicate that the adsorption process of $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ belongs to monolayer adsorption.

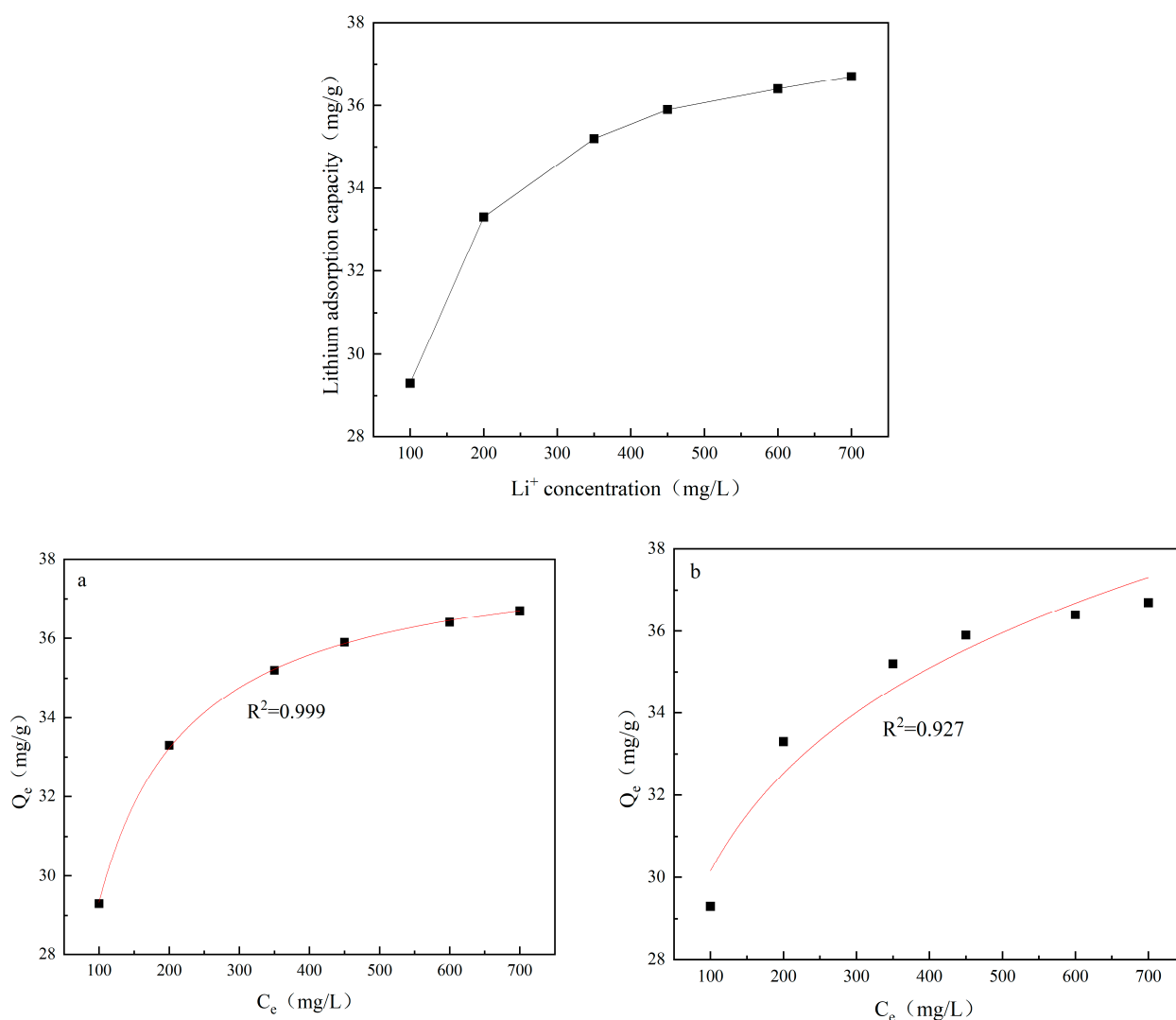


Figure 12. Adsorption isotherm and fitting results of the (a) Langmuir and (b) Freundlich equations.

5. Conclusions

Porous Mn_2O_3 was hydrothermally synthesized and calcined with Li_2CO_3 , using a carbothermal reduction-assisted solid-phase method to obtain LiMnO_2 . Subsequently, a lithium ion sieve was synthesized after roasting LiMnO_2 and acid pickling. The optimum synthesis conditions of LiMnO_2 are as follows: calcination temperature of 750°C , Li/Mn of 1.03, and addition of 5% glucose. The carbothermal reduction method protects manganese from oxidation and yields high-purity LiMnO_2 . The resulting Mn-based lithium ion sieve has an adsorption capacity of 35 mg/g . After five cycles, the dissolution percentage of Mn is stable at approximately 1%. Simultaneously, the adsorption capacity remains above 30 mg/g , demonstrating excellent cycling performance and structural stability.

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