

Synthesis of Lithium Ion Sieve Nanoparticles and Optimizing Uptake Capacity by Taguchi Method

Zandevakili, Saeed^{*+•}; Ranjbar, Mohammad

Department of Mining Engineering, Shahid Bahonar University of Kerman,
P.O. Box 76169-133 Kerman, I.R. IRAN

Ehteshamzadeh, Maryam

Department of Materials Engineering, Shahid Bahonar University of Kerman,
P.O.Box 76169-133 Kerman, I.R. IRAN

ABSTRACT: Spinel-type of MnO_2 nanoparticles which successfully synthesized by a hydrothermal process, have a required capacity for lithium uptake from liquid resources. The most lithium adsorption capacity of 6.6 mmol/g of up to now was found to be an important limiting parameter for industrial applications. Therefore, increasing uptake capacity of these ion sieves by studding the effect of six effective parameters, involving lithium compounds, manganese compounds, oxidizing reagents, calcination temperatures, heating times and Li/Mn mol ratios was investigated. To this end, Taguchi $L_9(3^4)$ orthogonal array was employed as a predominate method to evaluate these parameters and the results optimized by using analysis of variance (ANOVA) and analysis of mean (ANOM) in two separate stages. Although, all mentioned parameters had significant effect on lithium uptake capacity, but oxidizing reagents were the most effective factors. Hence, a new ion sieve with lithium adsorption capacity more than 9 mmol/g was synthesized for the first time, by applying this method.

KEY WORDS: Lithium, Ion sieve, Synthesis, Adsorption capacity, Taguchi experimental design.

INTRODUCTION

Hydrous oxides of tetravalent and pentavalent metals are known to possess interesting ion exchange properties [1]. Recently, ion-sieve type inorganic ion exchangers have attracted attention because of their remarkably high selectivity for certain ions [2]. Usually they can be prepared by the templating reaction, using metal ions as templates [2]. When lithium ions are used as templates, the inorganic exchangers obtained show remarkably high selectivity for the adsorption of lithium ions in the

aqueous phase. Many kinds of lithium ion-sieve materials such as spinel-type manganese oxide [3-5] titanic acid derived from Li_2TiO_3 , and monoclinic antimonite acid derived from $LiSbO_3$ have been developed to date [1].

Spinel-type manganese oxide can be obtained by heat treatment of Li^+ doped manganese oxide followed by the removal of Li^+ with acid. The Li^+ extraction/insertion reactions of spinel-type manganese oxides have been studied extensively from an applicable matter to the development

* To whom correspondence should be addressed.

+ E-mail: saeed.zandevakili@gmail.com

• New address: Department of Mining Engineering, Vali Asr University of Rafsanjan, P.O. Box 7718897111, Rafsanjan, Kerman, I.R. IRAN

1021-9986/14/4/15

10/\$/3.00

of electrode materials for lithium batteries [1, 6, 7] or lithium selective adsorbents from seawater [8, 9].

Spinel lithium manganese oxide can be expressed by the formula $(\text{Li})[\text{Li}_x\text{Mn}_{2-x}]\text{O}_4$, where () and [] represent 8a tetrahedral and 16d octahedral sites, whose oxygen atoms construct the cubic closed packed oxygen framework; x ranges from 0 to 0.33, forming a series of spinel Li-Mn oxides as LiMn_2O_4 , $\text{Li}_{1.14}\text{Mn}_{1.86}\text{O}_4$, $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$, etc [7].

Similarly, $\text{LiW}_{0.01}\text{Mn}_{1.99}\text{O}_4$ and $\text{LiU}_{0.01}\text{Mn}_{1.99}\text{O}_4$ as a potential candidate were considered for improvement of LiMn_2O_4 characterization and performance [10, 11]. In these samples, small amounts tungsten and uranium were incorporated into LiMn_2O_4 spinel instead of available manganese [11].

Over the past 20 years, numerous studies have been done on synthesis ion sieves with high Li^+ adsorption capacity [1, 6, 12-24]. The strongest of them with adsorption capacity of 6.6 mmol/g produced by *Sun et al.* in 2011 [23].

The investigations have shown that the structure and extraction/insertion reactions vary widely depending on the preparation methods and conditions.

Although the influence of some controlling parameter like Li/Mn mole ratio, calcination temperature or heating time on lithium ion sieve capacity investigated by different researchers, but there is no systematic study on these parameters and their effect. Also, the effects of some parameters like oxidizing reagent, lithium and manganese compounds have not been compared, yet. Therefore, in the present study, Taguchi method, as a combination of mathematical and statistical techniques, was used to optimize the experimental parameters for increasing lithium uptake capacity.

Taguchi method is a powerful tool for designing of experiments and determining the optimum test criteria. The method uses orthogonal arrays to obtain acceptable results with a smaller number of experiments. One of the important advantages of Taguchi method is analysis of qualitative and discrete factors. The most important step in Taguchi design method is to choose control parameters. Appropriate orthogonal array would then be selected based on the selected factors and their levels, and the experiments would be performed according to the proposed array [25-27]. Statistical method of Taguchi is proposed after identification of important as well as

effective factors usually through preliminary studies and experiments. After performing the experiments, results are to be analyzing through ANOVA (analysis of variance) to determine the partial contribution of each factor and the optimum conditions [28].

Moreover, this method presents the optimum experimental conditions and predicts the results based on the desired criteria [25, 28]. In this study, the contribution of the six controlled factors involving manganese compounds, lithium compounds, oxidizing reagents, Li/Mn mole ratios, calcination temperatures and heating times on the synthesized ion sieve was investigated. In summary, synthesis a new lithium ion sieve which improved characterization especially uptake capacity, was the main objective of the study.

EXPERIMENTAL SECTION

Synthesis of ion sieves

In this study, hydrothermal method was used as a predominate technique for synthesis lithium ion sieves. Synthesis process was done in three stages. At the first stage, MnO_2 nanoparticles were synthesized by mixing analytical grade manganese compounds (0.083 mol) with a stoichiometric ratio of Oxidizing reagents (0.083 mol) into 250 mL deionized water to form a homogeneous solution at room temperature, which was then transferred into a stainless steel autoclave, sealed, maintained for 12 h at 393 K. Subsequently, the resulted black product (named MO) was filtered, washed completely with deionized water to remove extra ions, and finally dried at 120 °C for 12 h in static air. In the second stage, Li-Mn-O precursor (named LMO) was prepared by wet impregnation of an aqueous solution of lithium compounds (0.5 mol/L with designed Li/Mn mol ratio) into MO black solid. Afterward, the mixture was heated to remove water at 120 °C, for 12 h in a drier and then calcination process at designed temperature and designed time was done. The third stage, involved Li^+ extraction from Li-Mn-O precursor which carried out by stirring LMO, in hydrochloric acid solution (0.5 mol.l⁻¹) for 48 h until the Li^+ ions were extracted. Finally, the acid-treated materials were filtered, washed with deionized water and dried at 120 °C for 12 h to obtain the proposed ion-sieve (named HMO).

Design of experiments

In this study, effects of different parameters on lithium uptake capacity of synthesized ion sieves

Table 1: Main controlling factors and their levels (First St.Exp).

Factors	Levels		
	1	2	3
Manganese compounds	MnSO ₄ .H ₂ O	MnCl ₂ .6H ₂ O	Mn(NO ₃) ₂ .4H ₂ O
Lithium compounds	LiOH	LiNO ₃	Li ₂ B ₄ O ₇
Li/Mn mol ratio	0.6	1	1.5

Table 2: Experimental condition based on Taguchi L₉(3⁴) array (First St.Exp).

Experiment Number	Manganese compounds	Lithium compounds	Li/Mn mol ratio
1	MnSO ₄ .H ₂ O	LiOH	0.6
2	MnSO ₄ .H ₂ O	LiNO ₃	1
3	MnSO ₄ .H ₂ O	Li ₂ B ₄ O ₇	1.5
4	MnCl ₂ .6H ₂ O	LiOH	1
5	MnCl ₂ .6H ₂ O	LiNO ₃	1.5
6	MnCl ₂ .6H ₂ O	Li ₂ B ₄ O ₇	0.6
7	Mn(NO ₃) ₂ .4H ₂ O	LiOH	1.5
8	Mn(NO ₃) ₂ .4H ₂ O	LiNO ₃	0.6
9	Mn(NO ₃) ₂ .4H ₂ O	Li ₂ B ₄ O ₇	1

were investigated. All experiments were conducted using Taguchi design method. Depending on the time and financial constraints, an appropriate level of input factors was selected. Experiments using Taguchi method allow several factors to be simultaneously determined effectively and efficiently. Afterward, the optimum level for each factor is determined and the best results can be predicted [25, 28].

In order to optimize the lithium adsorption capacity, total experiments were conducted in two stages. In the first stage of experiments, as shown in Table 1 three factors involving manganese compounds, lithium compounds and Li/Mn mol ratio in three levels were taken as variables and other parameters were fixed. To this end, (NH₄)₂S₂O₈ selected as oxidizing reagent and calcination temperature and heating time adjusted to 450 °C and 6 h respectively. Also orthogonal arrays of L₉(3⁴) was employed for this study, which could be observed in Table 2.

The effect of each control factor at a given level on lithium uptake was estimated and then the optimum levels of control factors with better yield obtained by analysis of mean (ANOM) [29, 30]. In order to estimate

how much the variance in lithium uptake is due to control factor or experiment error, the analysis of variance (ANOVA) was performed. Also the contribution percentage of each control factor was determined by this method [31]. Finally verification tests were conducted.

By optimizing manganese compounds, lithium compounds and Li/Mn mol ratio in the first stage of experiment, investigation on the other effective parameters including oxidizing reagents, calcination temperatures and heating times were conducted. Like the last test, these experiments were accomplished in three levels by L₉(3⁴) orthogonal arrays. The optimized factors in the first tests selected as fixed condition in the new tests. After determination of the optimum conditions, confirming test was carried out. In these tests, selected factors and levels could be observed in Table 3. Moreover, experimental conditions are presented in Table 4.

In this work, the lithium uptake was carried out by stirring (300 rpm) 100 mg of each ion sieve in 100 mL lithium enriched buffer solution (pH=11) with uniform initial Li⁺ concentration of 20 mmol/L at 25 °C and the Li⁺ concentration of supernatant solution was determined after 120 hours by ICP. (Q_e), the amount of Li⁺ adsorbed

Table 3: Main controlling factors and their levels (Second St.Exp).

Factors	Levels		
	1	2	3
Oxidizing reagents	Na ₂ S ₂ O ₈	(NH ₄) ₂ S ₂ O ₈	KMnO ₄
Calcination temperatures	450	500	550
Heating times	6	12	18

Table 4: Experimental condition based on Taguchi L9(3⁴) array (Second St.Exp).

Experiment Number	Oxidizing reagents	Calcination temperatures	Heating times
1	Na ₂ S ₂ O ₈	450	6
2	Na ₂ S ₂ O ₈	500	12
3	Na ₂ S ₂ O ₈	550	18
4	(NH ₄) ₂ S ₂ O ₈	450	12
5	(NH ₄) ₂ S ₂ O ₈	500	18
6	(NH ₄) ₂ S ₂ O ₈	550	6
7	KMnO ₄	450	18
8	KMnO ₄	500	6
9	KMnO ₄	550	12

Table 5: Results of First Stage of Experiments.

Experiment Number	Lithium adsorption (mmol/g)
1	5.89
2	7.44
3	2.33
4	1.96
5	3.24
6	1.47
7	3.56
8	8.49
9	2.4

per gram of ion sieve at equilibrium (mmol/g); was also calculated according to Eq. (1), in which; C_e , concentration of metal ions at equilibrium (L); C_0 , initial concentration of lithium ions (mmol/L); W , weight of adsorbent (g) and V , solution volume (mL) [17, 32]:

$$Q_e = (C_0 - C_e) \cdot \frac{V}{W} \quad (1)$$

RESULTS AND DESCUTION

First stage of experiment

The whole lithium uptake with synthesized ion sieves is listed in Table 5. The lithium adsorption capacity, ranges from 1.47 (mmol/g) to 8.49 (mmol/g). Table 6 shows the results of variance analysis (ANOVA).

In this Table, the sum of squares (SS_{Factor}), degrees of freedom (d_f) and mean of squares ($V = SS_{\text{Factor}}/d_f$) were represented, respectively. Subsequently, the F-value ($F_{\text{factor}} = V_{\text{factor}}/V_{\text{error}}$) and P-value were calculated. As illustrated in Table 6, F-value of the whole factors was greater than the extracted F-value of the Table for ($\alpha = 0.05$). It means that the variance of all factors is significant compared to the variance of error and all of them have a significant effect on the response. The significance of each coefficient was also determined by P-values, which are listed in this Table. P-values less than 0.05 indicate that model terms are significant. Consequently, the results of F-value and P-value confirm each other.

Table 6: Analysis of variance (First St.Exp). $F(0.05, 2, 2) = 19$.

	SS _{factor}	df	V	F-value	p-value	signafant
Model	51.9	6	8.65	61.24	0.0162	
Mn compounds	15.87	2	7.93	56.18	0.0175	
Li compounds	28.4	2	14.2	100.54	0.0098	
Li/Mn ratio	7.63	2	3.82	27.02	0.0357	
Error	0.28	2	0.14			
Total	52.18	8				

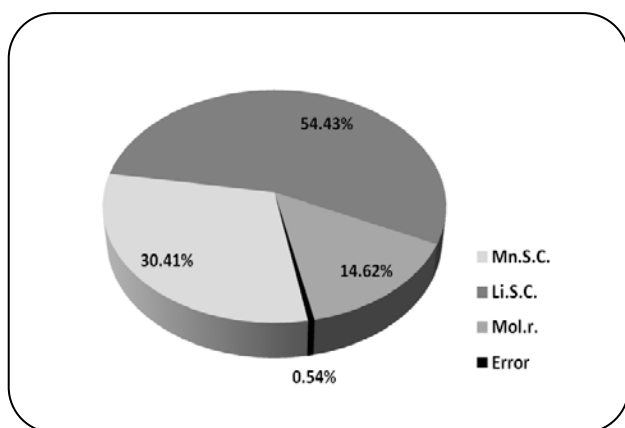


Fig. 1: Contribution of each factor on the response (First St.Exp).

Finally, the contribution of each factor to the synthesized ion sieves for lithium adsorption was determined as presented in Fig. 1. This analysis reveals that the order of factors that influences the lithium uptake is lithium compounds > manganese compounds > Li/Mn mol ratio, respectively. The error variance contribution is 0.55%. In other word, the experiment in this work has 99.45% of confidence if the interaction of factors isn't considered.

Fig. 2 shows the effect of each parameter level on the response variable, and demonstrates that the best adsorption obtained when manganese compounds was set at the first and the third, lithium compounds at the second, and Li/Mn mol ratio at the first levels.

Regarding manganese compounds, uptake of lithium ions increases in the order of $\text{MnCl}_2 \cdot 6\text{H}_2\text{O} < \text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} < \text{MnSO}_4 \cdot \text{H}_2\text{O}$. Additionally, concerning lithium compounds factor, increase in lithium adsorption follows the order of $\text{Li}_2\text{B}_4\text{O}_7 < \text{LiOH} < \text{LiNO}_3$ and it is the most significant factor. This reality could be satisfied by the fabrication of the strong acidity sites during

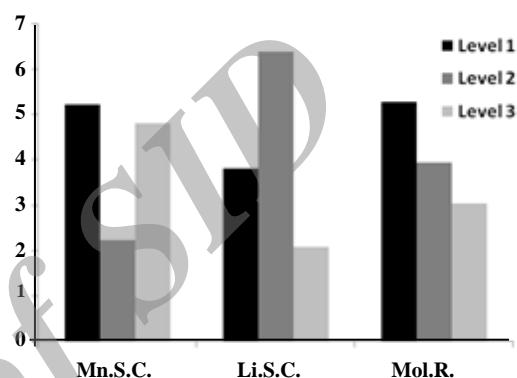


Fig. 2: Effect of each parameter level on the response variable (First St.Exp).

synthesis process. Generally, in equilibrium reaction $\text{R-H}^+ + \text{Li}^+ \rightleftharpoons \text{R-Li}^+ + \text{H}^+$ according to the Le Chatelier's principle, increasing the lithium uptake could be achieved by removing proton ions from medium solution, which could be attained by adding OH^- ions. Rising the solution pH or enhancing the intrinsic acidity of the exchange sites increase lithium ion adsorption. It seems that increase in intrinsic acidity of the ion sieve sites could be assigned to the nucleating pH during processing. Therefore strong acidity is advantageous for the sorption of lithium from a weakly basic solution like seawater [13, 23].

Furthermore, the effect of Li/Mn mol ratio is shown in Fig. 2. As it can be seen, increase in Li/Mn mole ratio decreases the lithium uptake. This could be satisfied by generation of different amount of impurity phase like Mn_2O_3 and Mn_3O_4 , especially when Li/Mn mole ratio is larger than 0.7. This fact is confirmed in a previously published litterateur [16].

Prediction of lithium uptake at optimized conditions was the last objective of the Taguchi statistical design and one of the most important goals of this research.

Table 7: Result of Second Stage of Experiments.

Experiment number	Lithium adsorption (mmol/g)
1	9.11
2	8.63
3	7.46
4	7.23
5	6.62
6	6.31
7	2.78
8	3.44
9	2.17

Table 8: Analysis of variance (Second St.Exp). $F(0.05, 2, 2) = 19$

	SS _{factor}	df	V	F-value	p-value	significant
Model	52.27	6	8.71	618.82	0.0016	
Oxidizing reagent	49.61	2	24.81	1762	0.0006	
Calcination temp	1.98	2	1	70.48	0.014	
Heating time	0.67	2	0.34	23.91	0.004	
Error	0.028	2	0.014			
Total	52.3	8				

Therefore, by determination of optimized factors and their levels, the optimized lithium ion sieve will be predicted by Eqs. (2) and (3) [26, 33].

$$\bar{Y} = \frac{\sum_{i=1}^n y_i}{n} = 4.086 \quad (2)$$

$$Y_{Opt} = \bar{y} + (A_1 - \bar{y}) + (B_2 - \bar{y}) + (C_1 - \bar{y}) = 8.7 \quad (3)$$

In Eq. (2) \bar{y} is the grand average of the responses and in Eq. (3) Y_{Opt} is the predicted surface area at optimum condition. After prediction, a verification test should be conducted. In this step, two samples were prepared under optimum condition (manganese compounds)_{1,3}, (lithium compound)₂, (Li/Mn mol ratio) [1] named 10, 11. The lithium uptake of samples 10 and 11 was measured as 7.64 and 8.56 mmol/g, respectively. Therefore, the best result formed under optimum condition (manganese compound₃, lithium compound₂, Li/Mn ratio₁) and the difference between

predicted (8.7 mmol/g) and the achieved values is negligible. The low error of (1.6%) confirms the predictability of the process and accuracy of the experimental results.

Second stage of experiment

As mentioned, these tests conducted by applying optimized condition from the previous tests. The whole lithium uptake with synthesized ion sieves under conditions presented in Table 4 is listed in Table 7. Table 8 shows the results of variance analysis. Comparing two F-value of factors and Table demonstrates that all parameters have a significant effect on the response.

The contribution of each factor on the synthesized ion sieves for lithium adsorption was shown in Fig. 3. This analysis reveals that the oxidizing agent as the main factor has the greatest impact on uptake capacity. Fig. 4 shows the effect of each parameter level on the response variable and demonstrates that the best uptake capacity obtained when all of factor set at their first levels. Then, the prediction of lithium uptake at optimized conditions

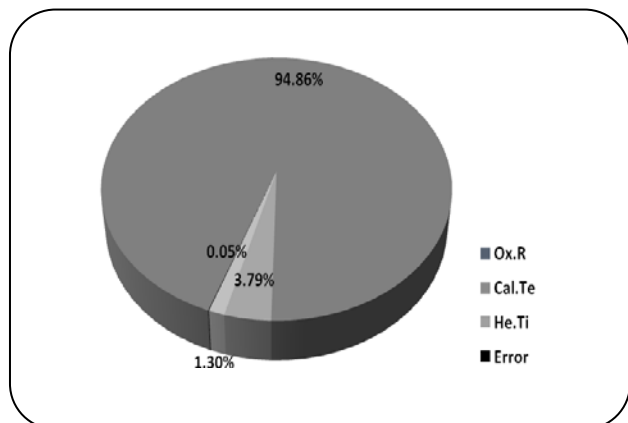


Fig. 3: Contribution of each factor on the response (Second St. Exp).

was conducted. By identifying the optimal parameters, the optimized ion sieve will be predicted by Eqs. (4) and (5).

$$\bar{Y} = \frac{\sum_{i=1}^n y_i}{n} = 5.97 \quad (4)$$

$$Y_{Opt} = \bar{y} + (A_1 - \bar{y}) + (B_2 - \bar{y}) + (C_1 - \bar{y}) = 9.11 \quad (5)$$

After prediction, a confirmation test conducted. In this step, a sample was prepared under optimum condition (Oxidizing reagent)₁, (Calcination temperature)₁, (Heating time)₁ named HMO_{Final}. The lithium uptake of this sample was measured 9.04 mmol/g. Since the difference between predicted (9.11 mmol/g) and the achieved values is negligible (0.07mmol/g) which shown the result is reliable.

Concerning Calcination temperature, increase in lithium adsorption follows the order of 550 °C < 500 °C < 450 °C. The extractability of lithium from heat-treated samples was investigated using a 0.5 M HCl solution. The Li⁺ extractability reached to 99.5% for the lithium manganese oxides obtained at 450 °C. But the extractability was decreased by increasing the calcination temperature for samples obtained above 450 °C, as only 88% of lithium ion could be extracted for the sample calcined at 550 °C. The difference in the lithium extractability may have been due to the differences in the lithium distribution in the solid depending on the heating temperature. Regarding Heating time, uptake of lithium ions increases in the order of 18 h < 12 h < 6 h. Therefore, it has confirmed the previous report, in which

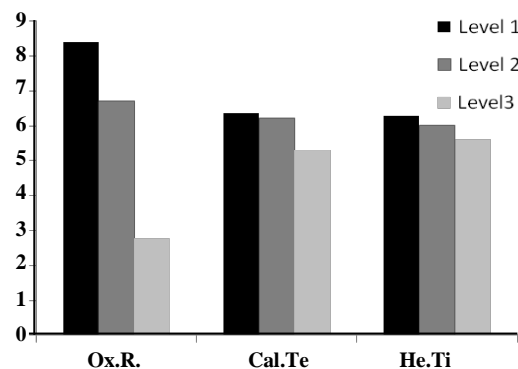


Fig. 4: Effect of parameter levels on the response variable (Second St. Exp).

increase in calcination time decreased the lithium uptake [16]. Although, increase in heating time improves the spinel phase crystalline, but increases the content of impurities especially Mn₂O₃ and Mn₃O₄. Formation of Mn₂O₃ impurity, with Li⁺ adsorption capacity less than 1.1 mg/g, could be the primary reason for decreasing Li⁺ uptake with the increase of heating time [16].

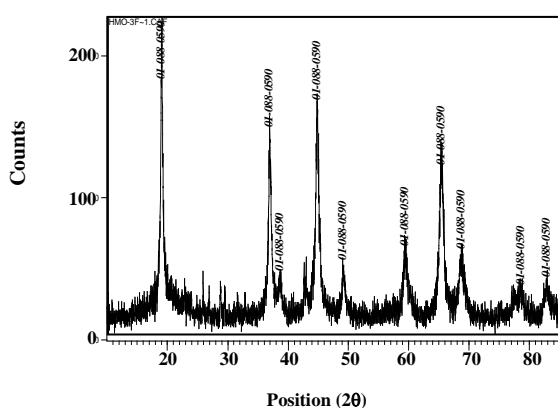
On the subject of oxidizing reagents factor, uptake of lithium ions increases in the order of KMnO₄ < (NH₄)₂S₂O₈ < Na₂S₂O₈. This could be satisfied by the electrochemical reactivity of synthesized powders resulted from different oxidizing agent. As increase in nanostructure MnO₂ electrochemical reactivity in alkaline medium leads to increase in ionic uptake capacity. Since the ion sieve synthesized by Na₂S₂O₈ is more reactive than the ion sieves synthesized by the other oxidizing reagent, uptake capacity increased in these samples [34]. In fact, difference in the MnO₂ electrochemical reactivity leads to the difference in the ion exchange capacity, because of the variety of structure, morphology, generated impurity, number and dimension of MnO₂ narrow sized tunnel [34]. Therefore MnO₂ with higher reactivity has more ion exchange capacity.

Comparison of lithium adsorbent

A comparison of lithium extraction from enriched liquid resources was made by different synthesized ion sieves from the past to present. According to this literature [1, 6, 12-24], the Li⁺ adsorption capacity of different synthesized ion sieves are listed in Table 9. According to it, achievement to adsorption capacity more

Table 9: Comparison of lithium uptake by different ion sieves and the synthesized ion sieve in this study.

Year	Lithium Uptake (mmol/g)	Ref.	Year	Lithium Uptake (mmol/g)	Ref.
1990	0.014	[12]	2009	5.33	[18]
2000	2	[1]	2010	5.38	[19]
2000	3.6	[13]	2010	3.42	[20]
2002	5.3	[13]	2010	5.57	[21]
2002	3.8	[15]	2010	1.53	[22]
2006	3.17	[16]	2010	2.91	[22]
2007	2.4	[6]	2011	6.67	[23]
2009	6.62	[17]	2013	>9	New sieve

**Fig. 5: XRD pattern of MnO₂ ion-sieve.**

than 9 mmol.g⁻¹ is possible by this new synthesized ion sieve. Furthermore, it shows that the adsorption capacity has been strengthened 35% compared to the best previous ion sieve.

XRD Result

Phase analyses of the new ion sieve (HMO_{Final}) are given in Fig. 5. The reflections of main peaks can be readily indexed to Li_{0.04}Mn₂O₄ phase [space group: Fd-3m (227), JCPDS 1-088-0590]. This means that, the removal of lithium ions from Li-Mn-O precursor structure during acid treatment is happen.

SEM and TEM Results

SEM result of new ion sieve (HMO_{Final}) is presented in Fig. 6. This prepared powder shows nanorod morphology with bulky aggregates.

Similarly, the TEM image of HMO sample which presented in Fig. 7, illustrates nanorods with an average

size of 50 nm in diameter and 800 nm in length. Smaller size provides bigger surface area and enhances the adsorption of Li⁺ ions. In addition, the high uptake rate and capacity can be related to the special particle structure of the ion sieve, especially smaller size in length. So, lithium ions can enter the pores from medium solution and cover the nanorod particles and because of ion sieve special structure, the path way between Li⁺ and H⁺ ions during the ion exchange process becomes shorter. Therefore, the ion exchange process can be performed easily.

CONCLUSIONS

In this study, an appropriate lithium ion sieve was synthesized via a hydrothermal process. The effects of six parameters including; manganese compounds, lithium compounds, Li/Mn mole ratio, oxidizing reagents, calcination temperatures and heating times in three levels on lithium adsorption capacity of synthesized ion sieves were investigated by L₉(3⁴) orthogonal arrays of Taguchi experimental design. ANOVA analysis was applied to evaluate the relative importance of the effects of various factors. From the results of this study, it can be concluded that lithium compounds and oxidizing reagents had the most significant effect on the lithium adsorption. The best ion sieve with maximum uptake capacity more than 9 mmol/g was synthesized by explained method in the presence of Mn(NO₃)₂.4H₂O as manganese compounds, LiNO₃ as lithium compounds, Na₂S₂O₈ as oxidizing reagent, Li/Mn mole ratio equal to 0.6, calcination temperature and heating time adjusted to 450 °C and 6 hours, respectively. Therefore, lithium uptake capacity increased 35% relative to the best condition in the past.

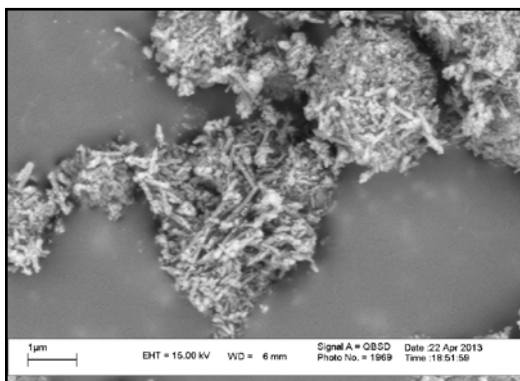


Fig. 6: SEM image of MnO_2 ion-sieve.

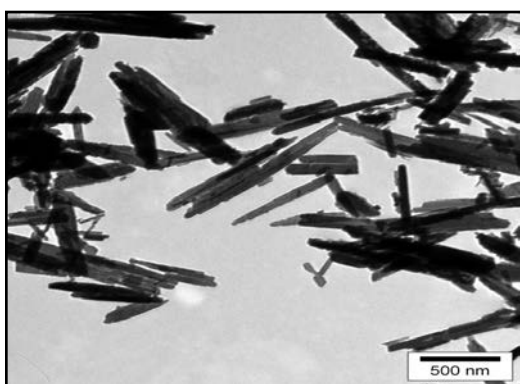


Fig. 7: TEM image of MnO_2 ion-sieve

Received : Feb. 22, 2014 ; Accepted : Aug. 25, 2014

REFERENCES

- [1] Chitrakar R., Kanoh H., Makita Y., Miyai Y., Ooi K., Synthesis of Spinel-Type Lithium Antimony Manganese Oxides and Their Li Extraction/Ion Insertion Reactions, *J Mater Chem.*, **10** (10): 2325-2329 (2000).
- [2] Feng Q., Kanoh H., Miyai Y., Ooi K., Hydrothermal Synthesis of Lithium and Sodium Manganese Oxides and Their Metal Ion Extraction/Insertion Reactions, *Chem Mater.*, **7**: 1226-1232 (1995).
- [3] Hunter J.C., Preparation of a New Crystal form of Manganese Dioxide: λ - MnO_2 , *J. Solid State Chem.*, **39**: 142-7 (1981).
- [4] Ooi K., Miyai Y., Katoh S., Recovery of Lithium from Seawater by Manganese Oxide Adsorbent, *Sep Sci Technol.*, **21**: 755-766 (1986).
- [5] Shen X.M., Clearfield A., Phase Transitions and Ion Exchange Behavior of Electrolytically Prepared Manganese Dioxide, *J Solid State Chem.*, **64**(3): 270-282 (1986).
- [6] Zhang Q.H., Sun S., Li S., Jiang H., Yu J.G., Adsorption of Lithium Ions on Novel Nanocrystal MnO_2 , *Chem Eng Sci.*, **62**(18-20): 4869-4872 (2007).
- [7] Zhang Q.H., Li Sh., Sun S.Y., Yin X.S., Yu J.G., $LiMn_2O_4$ Spinel Direct Synthesis and Lithium ion Selective Adsorption, *Chem Eng Sci.*, **65**(1): 169-173 (2010).
- [8] Miyai Y., Ooi K., Katoh S., Recovery of Lithium from Seawater Using a New Type of Ion-Sieve Adsorbent Based on $MgMn_2O_4$, *Sep. Sci. Technol.*, **23**(1-3): 179-191 (1988).
- [9] Khamizov R. Kh., Mironova L.I., Tikhonov N.A., Bychkov A.V., Poezd, A.D. Recovery of Pure Magnesium Compounds from Seawater by the Use of the Effect of Isothermal Supersaturating in the Ion-Exchange Process, *Separation Science and Technology*, **31**: 1-20 (1996).
- [10] Eftekhari A., Bayandori Moghaddam A., Yazdani B., Moztarzadeh F., Effects of Metal Source in Metal substitution of Lithium Manganese Oxide Spinel, *Electrochimica Acta.*, **52**: 1491-6 (2006).
- [11] Eftekhari A., Bayandori Moghaddam A., Solati-Hashjin M., Electrochemical Properties of $LiMn_2O_4$ Cathode Material Doped with an Actinide, *Journal of Alloys and Compounds.*, **424**: 225-230 (2006).
- [12] Kaneko S., Takahashi W., Adsorption of Lithium in Sea water on Alumina Magnesia Mixed-Oxide Gels, *Colloids and Surfaces*, **47**: 69-79 (1990).
- [13] Chitrakar R., Kanoh H., Miyai Y., Ooi K., A New Type of Manganese Oxide ($MnO_2 \cdot 0.5H_2O$) Derived from $Li_1.6Mn_1.6O_4$ and Its Lithium Ion-Sieve Properties, *Chemistry of Materials*, **12**(10): 3151-7 (2000).
- [14] Chitrakar R., Kanoh H., Miyai Y., Ooi K., Recovery of Lithium from Seawater Using Manganese Oxide Adsorbent ($H_{1.6}Mn_{1.6}O_4$) Derived from $Li_1.6Mn_{1.6}O_4$, *Industrial & Engineering Chemistry Research*, **40**(9): 2054-8 (2001).
- [15] Lei J.h., Chen Y.x., Gong Q.x., Sun Y.b., Zhao J., Yuan Q-h., Preparation of λ - MnO_2 by Column Method and its Ion-sieve Property, *Journal of Wuhan University of Technology-Mater. Sci. Ed.*, **17**(4): 9-12 (2002).

- [16] Wang L., Ma W., Liu R., Li H.Y., Meng C.G., Correlation Between Li⁺ Adsorption Capacity and the Preparation Conditions of Spinel Lithium Manganese Precursor, *Solid State Ionics.*, **177**(17–18): 1421-1428 (2006).
- [17] Zhang Q.H., Li Sh., Sun S.Y., Yin X.S., Yu J.G., Lithium Selective Adsorption on 1-D MnO₂ Nanostructure Ion-Sieve, *Advanced Powder Technology*, **20**(5): 432-437 (2009).
- [18] Wang L., Meng C., Ma W., Preparation of Lithium Ion-Sieve and Utilizing in Recovery of Lithium from Seawater, *Frontiers of Chemical Engineering in China*, **3**(1): 65-67(2009).
- [19] Tian L., Ma W., Han M., Adsorption Behavior of Li⁺ onto Nano-Lithium Ion Sieve from Hybrid Magnesium/Lithium Manganese Oxide, *Chemical Engineering Journal*, **156**(1): 134-140 (2010).
- [20] Zhang Q.H., Li Sh., Sun S.Y., Yin X.S., Yu J.G., Lithium Selective Adsorption on Low-Dimensional Titania Nano Ribbons, *Chemical Engineering Science*, **65**: 165-168 (2010).
- [21] Özgür C., Preparation and characterization of LiMn₂O₄ Ion-Sieve with High Li⁺ Adsorption Rate by Ultrasonic Spray Pyrolysis, *Solid State Ionics*, **181**(31–32): 1425142-8 (2010).
- [22] Ma L.W., Chen B.Z., Shi X.C., Zhang W., Zhang K., Stability and Li⁺ Extraction/Adsorption Properties of LiM_xMn_{2-x}O₄ (M=Ni, Al, Ti; 0 ≤ x ≤ 1) in Aqueous Solution, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **369**(1–3): 88-94 (2010).
- [23] Sun S.Y., Song X., Zhang Q.H., Wang J., Yu J.G., Lithium Extraction/Insertion Process on Cubic Li-Mn-O Precursors with Different Li/Mn Ratio and Morphology, *Adsorption* **17**(5): 881-887 (2011).
- [24] GargGagandeep T., RathGoutam, M.B., Development and Characterization of Nano-Fiber Patch for the Treatment of Glaucoma, *European Journal of Pharmaceutical Sciences*, In Press (2013).
- [25] Rouhi A.R., Fatehifar E., Application of New Application of New Inflection Point Method for Hydrodynamics Study in Slurry Bubble Column Reactors, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **32**(2): 81-92 (2013).
- [26] Roy R.K., "Design of Experiments Using The Design of Experiments Using The Taguchi Approach: 16 Steps to Product and Process Improvement, *John Wiley & Sons*, London 450-480 (2001).
- [27] Khosravi-Darani K., Vasheghani-Farahani E., Application of the Taguchi Design for Production of Poly(β-Hydroxybutyrate) by *Ralstonia Eutropha*, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **23**(1): 131-136 (2004).
- [28] Pourjavadi A., Soleyman R., Novel High Capacity Swelling Superabsorbent Composite and Its Potential for Controlled Release of Fertilizers, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **29**(4): 113-123 (2010).
- [29] Liu W.L., Hsieh S.H., Chen W.J., Lee J.H., Study of Study of Nanosized Zinc Oxide on Cu-Zn Alloy Substrate Using Taguchi Method, *Surface and Coatings Technology.*, **201**(22–23): 9238-9242 (2007).
- [30] Chou C.S., Yang R.Y., Chen J.H., Chou S.W., The Optimum Conditions for Preparing the Lead-Free Piezoelectric Ceramic of Bi_{0.5}Na_{0.5}TiO₃ Using the Taguchi Method, *Powder Technology*, **199**(3): 264-271 (2010).
- [31] Tofighy M., Ahmadzadeh S., Mohammadi T., Salty Water Desalination Using Carbon Nanotube Sheets, *Desalination*, **258**(1): 182-186 (2010).
- [32] Ma L.W., Chen B.Z., Shi X.C., Zhang W., Zhang K., Stability and Li⁺ Extraction/Adsorption Properties of LiM_xMn_{2-x}O₄ (M= Ni, Al, Ti; 0≤x≤1) in Aqueous Solution, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **369**: 88-94 (2010).
- [33] Norouzbeigi R., Edrissi M., Modification and Optimization of Nano-Crystalline Al₂O₃ Combustion Synthesis Using Taguchi L16 Array, *Materials Research Bulletin*, **46**(10): 1615-1624 (2011).
- [34] Benhaddad L., Makhloufi L., Messaoudi B., Rahmouni K., Takenouti H., Reactivity of Nanostructured MnO₂ in Alkaline Medium Studied with a Microcavity Electrode: Effect of Oxidizing Agent, *Journal of Materials Science & Technology*, **27**(7): 585-593 (2011).