

Synthesis of $\text{Li}_{1.6}[\text{MnM}]_{1.6}\text{O}_4$ (M=Cu, Ni, Co, Fe) and Their Physicochemical Properties as a New Precursor for Lithium Adsorbent

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$\text{Li}_{1.6}[\text{MnM}]_{1.6}\text{O}_4$ (M=Cu, Ni, Co, Fe)의 합성 및 리튬 흡착제용 신규 전구체로서의 물리화학적 성질

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Abstract New precursors as a Li adsorbent, $\text{Li}_{1.6}(\text{MnM})_{1.6}\text{O}_4$ (M=Cu, Ni, Co, Fe), were synthesized by hydrothermal method and their physicochemical properties were discussed. XRD and HRTEM results revealed that the original spinel structure was stabilized by cobalt-doping while Cu-, Ni- and Fe-doping led to structural changes. Such a structural stabilization by Cobalt-doping was maintained after lithium leaching by acid treatment. Li absorption efficiency from seawater was significantly enhanced by using the Cobalt-doped spinel manganese oxide, $\text{Li}_{1.6}[\text{MnCo}]_{1.6}\text{O}_4$, compared to the commercially available $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$; the adsorbed amount of Li from 1g-adsorbent was 35 and 16 mg by $\text{Li}_{1.6}[\text{MnCo}]_{1.6}\text{O}_4$, and $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$, respectively.

요약 리튬 흡착제용 신규 전구체인 $\text{Li}_{1.6}(\text{MnM})_{1.6}\text{O}_4$ (M=Cu, Ni, Co, Fe)을 수열법에 의해 합성한 후에, 물리화학적인 성질을 고찰하였다. XRD와 HRTEM을 이용한 분석 결과로부터 Co를 도핑한 경우에는 본래의 스핀넬 구조가 유지되는 반면에, Cu, Ni, Fe를 도핑한 경우에는 구조적인 변화가 발생하는 것을 확인하였다. Co 도핑에 의해 확인된 구조의 안정화는 산처리 후에도 리튬을 침출시킨 후에도 유지되었다. 해수에 함유된 리튬을 흡착하는 효율은 Co가 도핑된 망간 산화물인 $\text{Li}_{1.6}[\text{MnCo}]_{1.6}\text{O}_4$ 가 상업적으로 적용 가능한 $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ 보다 우수한 특성을 나타내었다. 해수 1g으로부터 흡착되는 Li의 양은 $\text{Li}_{1.6}[\text{MnCo}]_{1.6}\text{O}_4$ 를 사용했을 경우에 35mg이었고, $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ 를 사용했을 경우에는 16mg 이었다.

Key Words : Li-adsorbent, Spinel-type manganese oxide. Co-dopant, Li absorption efficiency

1. Introduction

Lithium is a soft, silver-white metal that belongs to the alkali metal group of chemical elements. It is a very

important element as raw materials in several industrial fields, e.g., ceramics, lithium batteries, lubricating greases, coolant adsorbent, pharmaceuticals *etc.* Recently, there is an increasing demand for further lithium production

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because of the widespread hopes of using rechargeable lithium batteries in electric vehicles and dispersed energy storage systems. However, the whole amount of lithium from the land is limited. Therefore, alternative resources should be found to satisfy the increasing demands. Seawater, which contains 250 billion tons of lithium in total, has thus recently been noticed as possible resources of lithium.

It is a very useful and promising method to use adsorbents that has the high selectivity for lithium ion for recovering the lithium from the seawater. Lithium manganese oxides with spinel structure have been extensively investigated as adsorption materials for lithium [1-6]. Materials such as γ - MnO_2 , $\text{H}_{1.33}\text{Mn}_{1.67}\text{O}_4$, and $\text{MnO}_2 \cdot 0.5\text{H}_2\text{O}$ derived from the precursors LiMn_2O_4 , $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ and $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$, respectively, are known as lithium ion selective adsorbents [7-14].

In this work, new precursors $\text{Li}_{1.6}(\text{MnM})_{1.6}\text{O}_4$ (M=3d transition metal) with spinel structure were prepared by hydrothermal method. Their structure and chemical properties as a precursor of lithium adsorbent were analyzed and discussed.

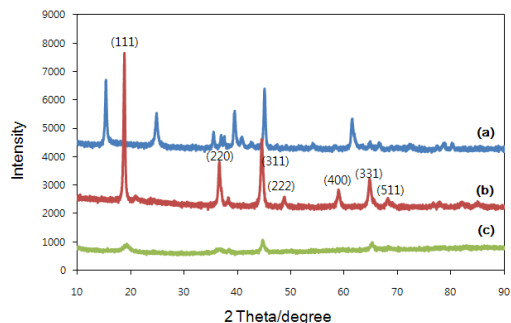
2. Experimental

Reagent grade LiOH and γ - MnOOH were used as starting materials to synthesize orthorhombic LiMnO_2 by hydrothermal method. Then the LiMnO_2 was calcined at 450°C for 10 hours in air with or without transition metal to get $\text{Li}_{1.6}(\text{MnM})_{1.6}\text{O}_4$ (M=3d transition metal). Lithium ion-sieve, $\text{H}_{1.6}(\text{MnM})_{1.6}\text{O}_4$, was obtained by leaching the $\text{Li}_{1.6}(\text{MnM})_{1.6}\text{O}_4$ with dilute hydrochloric acid (below 1 mol dm^{-3}). The structural information of the $\text{Li}_{1.6}(\text{MnM})_{1.6}\text{O}_4$ was obtained with X-ray Diffractometer (XRD, Panalytical Xpert-MPD coupled with a $\text{Cu-K}\alpha$ radiation tube) and high resolution transmission electron microscopy (HRTEM, JEOL, JEM-2100F). The extraction of lithium ion from the $\text{Li}_{1.6}(\text{MnM})_{1.6}\text{O}_4$ was achieved by acid-treatment to get the information on acid intensity of lithium ion. The $\text{Li}_{1.6}(\text{MnM})_{1.6}\text{O}_4$ powder was dissolved in a mixture of H_2SO_4 and H_2O_2 . And then each content of lithium, transition metal and manganese in the $\text{Li}_{1.6}(\text{MnM})_{1.6}\text{O}_4$ was determined by AAS(atomic absorption spectrometry) and inductively coupled plasma coupled

mass spectrometer (ICP-AES) from the solution. The available oxygen of each sample was determined by the standard oxalic acid method [15]. The mean oxidation number (Z_{Mn}) of manganese was evaluated as described in the literature [6].

3. Results and Discussion

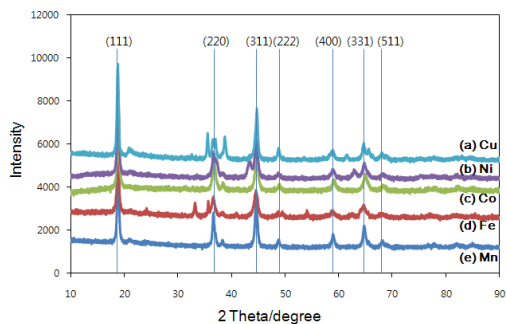
In order to know the structure of the synthesized $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ and its structural stability of after leaching, X-ray diffractions have been performed, as shown in Fig. 1. The indexing results indicate that the $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ (Fig. 1(b) obtained by calcination of LiMnO_2 (Fig. 1(a) has a spinel structure. The intensity and sharpness of the spinel peaks greatly decreased, as shown in Fig. 3(c), after lithium was leached out from the $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ by acid treatment. This means that the structural stability is not good, and the $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ given by acid treatment is not effective as a lithium adsorbent. In other words, the quality of the synthesized $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ as a precursor is not good. To improve the precursor performance, Mn was substituted by other 3d transition metals such as Cu, Ni, Fe, Co.



[Fig. 1] XRD patterns of the (a) LiMnO_2 , (b) $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ and (c) acid-treated $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$.

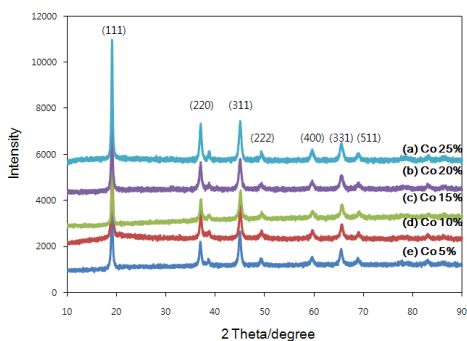
Figure 2 shows the XRD patterns of the 3d transition metal-doped $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$. The spinel structure of the $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ was not changed by Cobalt doping (Fig 2(c), whereas new XRD peaks originating from structural changes were observed in the case of Cu or Ni or Fe doping (Fig. 2(a), (b), (d)). The Cobalt ions are located in 16d octahedron site of Mn, which is in fair agreement with that of the cubic structure (space group $Fd\bar{3}m$).

This results clearly reveals that Cobalt is very effective as a doping element because the spinel is a favorable structure to precursor as a lithium adsorbent.



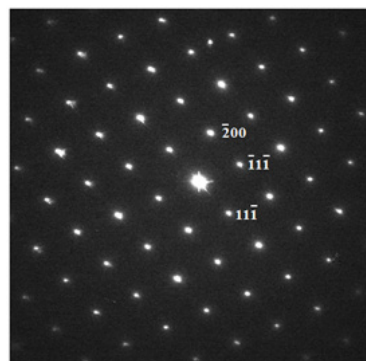
[Fig. 2] XRD patterns of 3d transition metal-doped $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$.

On the basis of the XRD results shown in Fig. 2, Cobalt is selected as a dopant toward $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$. The content of Cobalt was between 5 and 25 %. In the content range, no structural changes in the Cobalt-doped $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ powders were observed from its XRD (not shown here). Lithium was leached out from the Cobalt-doped $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ powders by acid treatment, and then XRD analysis was performed to know their chemical property as a precursor of Li adsorbent. Their XRD patterns are shown in Fig. 3. All the peaks were in fair agreement with those of cubic structure of $Fd\bar{3}m$. Also they could be marked with $Fd\bar{3}m$ of spinel structure. Thus it is considered that the Cobalt-doped $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ powders after acid treatment have a well arranged spinel structure. These XRD results indicate that Li maintains the spinel structure, when it goes into the Mn site.



[Fig. 3] XRD patterns of Cobalt-doped $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ after acid treatment.

Additional information on the structure of the Cobalt-doped $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ was confirmed with HRTEM. Figure 4 shows a electron diffraction pattern taken from the sample of $\text{Li}_{1.6}[\text{MnCo}]_{1.6}\text{O}_4$. As the result of phase identification of Fig.4, this pattern was identified as $B=[011]$ of the single crystalline having spinel structure ($a=8.2 \text{ \AA}$).



Spinel structure, $B=[011]$, $a=8.2$

[Fig. 4] An HRTEM image of the $\text{Li}_{1.6}[\text{MnCo}]_{1.6}\text{O}_4$.

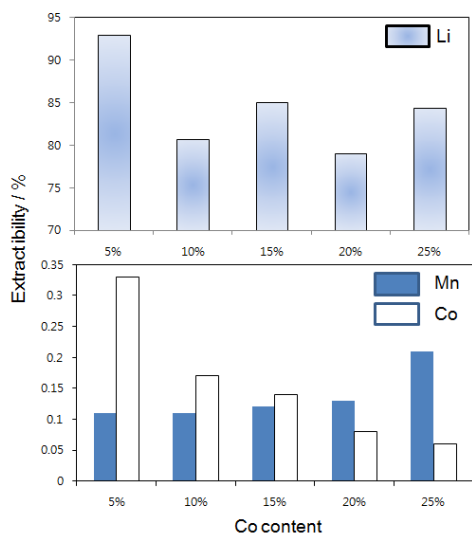
Chemical analysis was carried out with an AAS and ICP-AES system to know the performance as a adsorbent according to the amount of Cobalt doping. Metal ion eruption in the samples proceeded in 0.5 mol dm^{-3} HCl aqueous solution for 3 days. The AAS and

ICP-AES results are shown in Table 1. It is known that appropriate oxidation number of Mn is +4 for high qualified lithium adsorbent. Therefore, the AAS and ICP-AES results, those are close to +4, indicate that the $\text{Li}_{1.6}[\text{MnCo}]_{1.6}\text{O}_4$ is a good precursor. Consequently Cobalt could be ionized best of all in 3d transition metal used in this work. Lithium ion extracted from $\text{Li}_{1.6}[\text{MnCo}]_{1.6}\text{O}_4$ spinel was produced by ion exchange method. This result shows that lithium ion was extracted selectively from this materials.

[Table 1] Chemical composition for the original and acid-treated sample

Sample	Chemical Formula	Average Oxidation state of Mn
Li^+ type		
$\text{Li}_{1.6}[\text{MnCo}]_{1.6}\text{O}_4$	$\text{Li}_{2.1}\text{Mn}_{1.37}\text{Co}_{0.15}\text{O}_4$	3.87
H^+ type		
$\text{Li}_{1.6}[\text{MnCo}]_{1.6}\text{O}_4$	$\text{Li}_{0.08}\text{Mn}_{1.32}\text{Co}_{0.18}\text{O}_4$	3.75

Figure 5 shows the extractability of the $\text{Li}_{1.6}[\text{MnCo}]_{1.6}\text{O}_4$ spinels. To extract the lithium ion and 3d transition metal from the spinels, the samples were soaked in the HCl aqueous solution for 3 days. The amount of extracted manganese ion was quite small compared to that of lithium ion. The ability of extraction of lithium ion has an increasing tendency with the decrease of the amount of Cobalt-doping. The amount of Li adsorbed was estimated to be 35 mg per 1g-adsorbent from Fig. 5. This value is much larger than that obtained by commercially available $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$, in which a relatively small amount of Li (16 mg per 1g-adsorbent) was adsorbed.



[Fig. 5] Extractability of the acid-treated Cobalt-doped $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$.

4. Conclusions

In this work, a spinel-type manganese oxide, $\text{Li}_{1.6}[\text{MnCo}]_{1.6}\text{O}_4$, was synthesized by hydrothermal method with good reproducibility. The $\text{Li}_{1.6}[\text{MnCo}]_{1.6}\text{O}_4$ showed extraordinarily excellent property as a new precursor of Li adsorbent.

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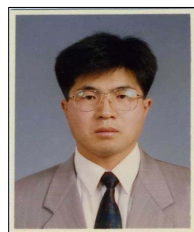


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