Effect of Acid Treatment on Removing Sodium Ions from Sodium Cobalt Oxide Thermoelectric Materials

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Abstract: Na₈Co₄O₁₄ with a laminar structure is a promising thermoelectric oxide having anisotropic thermoelectric property. An excellent thermoelectric performance equivalent to the single crystal is expected to be attainable in the polycrystalline body of this material by improvement of crystal orientation. It will be effective for controlling the crystal orientation to separate CoO₂ nanosheets from the polycrystalline body and to pile them up for making highly orientated layers. We aim at preparation of the CoO₂ nanosheets. First, samples of Na₈Co₄O₁₄ were synthesized. The interlayer Na⁺ ions were removed from the CoO₂ layers of the synthesized powder by an acid treatment. The interlayer distance of the synthesized and the Na⁺ ion removed samples was measured by XRD analysis. The removal efficiency of Na⁺ ions was evaluated from ICP measurement. The morphology of the samples was observed by a SEM. We found that the condition of the acid treatment greatly influences the removal efficiency of Na⁺ ions in the synthesized Na₈Co₄O₁₄.

Keywords: Thermoelectric sodium cobalt oxide, Nanosheet, Acid treatment, Removal efficiency

1. INTRODUCTION
Thermoelectric power generation that can directly convert thermal energy into electrical energy through the Seebeck effect has been expected as a promising energy conversion technique to achieve energy savings and the effective use of waste heat exhausted by automobiles and incinerators. The performance of thermoelectric materials is evaluated by the dimensionless figure of merit $ZT$ that is defined as $ST\rho/k$, where $S$ is the Seebeck coefficient (V/K), $\rho$ is the electrical resistivity (\Omega/m), $k$ is the thermal conductivity (W/mK) and $T$ the absolute temperature (K), respectively. For obtaining a high thermoelectric performance, materials having larger $S$, lower $\rho$ and lower $k$ are required.

Recently, several electronic conductive oxides, such as (Zn₁₋ₓAlₓ)O, BaSrPbO₃, Na₂Co₄O₉, Ca₂Co₄O₉ and SrTiO₃ systems, have been recognized as the potential candidates for thermoelectric materials.[1-9] These thermoelectric oxides can be used at high temperature without deterioration of their performance due to oxidation, and their production costs are comparatively low. Na₈Co₄O₁₄ thermoelectric material is a layered oxide composed of an electric conductive CoO₂ layer and an insulating Na layer, which are perpendicular to the c-axis. (Fig. 1) The electrical resistivity along its c-axis is about 10 times larger than that along its a-plane.

Omomo et al. (2002) reported that manganese nanosheets with a laminar structure like Na₂Co₄O₉ can be made by exfoliating the laminar structure. [10] From these facts, an excellent thermoelectric performance equivalent to the single crystal is expected to be attainable in the polycrystalline body of this material by improvement of crystal orientation. It will be effective for controlling the crystal orientation to separate CoO₂ nanosheets from the polycrystalline body and to pile them up for making highly orientated layers. We aim at preparation of the cobalt oxide nanosheets. In this study, as the first stage of a series of studies for making the cobalt oxide nanosheets, we attempted to remove the layers of sodium ions for preparation of exfoliation reactions. The polycrystalline samples of sodium cobalt oxide were synthesized. The sodium ions were removed from the cobalt oxide layers of the synthesized powder by an acid treatment. The interlayer distances of the synthesized and Na⁺-removed samples were measured. The removal efficiency of Na⁺ ions was evaluated and the effect of the acid treatment on the removal efficiency of Na⁺ ions was focused.

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The mixture was calcined at 1073K for 20h in air.
In order to remove the layers of Na ions by acid treatment, the calcined Na₃Co₃O₅ (x=0.58) powder was soaked in a solution of HCl, H₂SO₄ or HNO₃ (0.5M~2.0M) for 1day. The grinding of the calcined Na₃Co₃O₅ powder with the planetary ball mill for 1h and the repeating of the acid treatment in H₂SO₄ solution (0.5M) for 1day were also attempted to improve the removal efficiency of Na⁺ ions.

The phases of the calcined samples were identified by X-ray diffraction (XRD). The morphology of the samples was observed by a scanning electron microscope (SEM). The molar ratio of metal ions in the samples was chemically analyzed by inductively coupled plasma atomic-emission spectrometry (ICP-AES).

3. RESULT AND DISCUSSION
3.1. Influences of type and concentration of acid on removing of Na⁺ ions

Figure 1 shows the SEM images of the calcined samples (a) before acid treatment, (b) after acid treatment in 0.5M H₂SO₄ solution, respectively. The samples were composed of platelike crystals with a lateral dimension of micrometers.

Figure 2 shows the XRD patterns of the calcined samples (a) before acid treatment, (b) after once acid treatment in 0.5M HCl solution, (c) after twice acid treatments in 0.5M HCl solution, respectively. The samples were sifted to the lower diffraction angle. This indicates the increase in distance between CoO₂ layers by the substitution of H₂O⁺ ions for Na⁺ ions.

Table 1 lists the removal efficiency of Na⁺ ion. There are no large differences in the removal efficiency of Na⁺ ion among the samples after the acid treatments. This indicates that the type and a concentration of acid have no significant effect on the removal of Na⁺ ions from the interlayer of CoO₂.

<table>
<thead>
<tr>
<th>Acid solution</th>
<th>Removal efficiency of Na⁺ ion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5M HCl</td>
<td>56.0</td>
</tr>
<tr>
<td>1.0M HCl</td>
<td>59.2</td>
</tr>
<tr>
<td>2.0M HCl</td>
<td>57.2</td>
</tr>
<tr>
<td>0.5M HNO₃</td>
<td>52.5</td>
</tr>
<tr>
<td>1.0M HNO₃</td>
<td>53.2</td>
</tr>
<tr>
<td>2.0M HNO₃</td>
<td>54.6</td>
</tr>
<tr>
<td>0.5M H₂SO₄</td>
<td>55.4</td>
</tr>
<tr>
<td>1.0M H₂SO₄</td>
<td>59.7</td>
</tr>
<tr>
<td>2.0M H₂SO₄</td>
<td>52.6</td>
</tr>
</tbody>
</table>

3.2. Influence of repetition of acid treatment on removal of Na⁺ ions

Figure 3 shows the XRD patterns of the calcined samples (a) before acid treatment, (b) after once acid treatment in 0.5M H₂SO₄ solution and (c) after twice acid treatments in 0.5M H₂SO₄ solution, respectively.

At the XRD pattern of the sample after twice acid treatments, a main peak shifted to the higher diffraction angle. This suggests the decrease in distance between CoO₂ layers by the substitution of H⁺ ions for Na⁺ ions. The removal efficiency of Na⁺ ion in the sample after twice acid treatments was 75~94 %. Thus, it is clear that...
the repetition of the acid treatment contributes to elevate the removal efficiency.

![Graph showing XRD patterns](image)

Fig. 4 Influences of repetition of acid treatment on XRD patterns (a) before acid treatment, (b) after once acid treatment in 0.5 M H₂SO₄ solution, (c) after twice acid treatment in 0.5 M H₂SO₄ solution

3.3. Effect of mechanical grinding on Na⁺ ion removal.

In order to investigate an influence of mechanical grinding (MG) on the Na⁺ ion removal, the calcined samples without and with MG for 1h were prepared and then applied to the acid treatment. Figure 4 shows the SEM images of the samples (a) without MG, (b) with MG for 1h. In the MG sample, we can recognize that the crystals are crashed by MG. The removal efficiency of Na⁺ ion in the MG sample was about 70%. It is, therefore, clear that the mechanical grinding improves the removal efficiency of Na⁺ ion. The reason for this is likely that the increase in reaction area of the crystal crushed by MG contributes the removal of Na⁺ ions.

4. CONCLUSION

In this study, the influences of different conditions on the removal of Na⁺ ions from the interlayer of CoO₂ were investigated for preparation of exfoliation reaction. The results are summarized as follows,

1. The type and concentration of acid do not affect the removal of Na⁺ ions.
2. The repetition of the acid treatment improves removal efficiency of Na⁺ ions.
3. The mechanical grinding of the calcined samples promotes the removal of Na⁺ ions.
4. The maximum removal efficiency of 94% was attained after twice acid treatments in 0.5M H₂SO₄ solution was 94%.

REFERENCES