<table>
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<th>Development of Inorganic Green Materials using Redox Property</th>
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<tr>
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<td>Nagashima, Kohji</td>
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Development of Inorganic Green Materials

using Redox Property

Kohji Nagashima

2015
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**General Introduction**

1 Preliminary

An expansion of demand for energy and raw materials of humanity is gradually boosting up natural resources to their limits, giving rise to more environmental problems. [1] However, this requisition is an essential component of society. In regard to this point, chemistry has played an important role. Inorganic chemistry is the research of the structure, synthesis and behavior of inorganic or organometallic materials. Almost every sector of the chemical industry makes use of inorganic chemistry, including fuels, energy storage, catalysis, materials science and more. Owing to this academic discipline, functional materials, which have been greatly developed for decades, are becoming more and more important as key factors for building a sustainable society. Developing novel functional material is consistently required for resolution of energy resources shortage and global environmental problems, and for improvement of comfort and convenience in the society.

2 Background

2.1 Hydrogen

Subsequently to coal and oil, hydrogen will play a very crucial role as energy source. Hydrogen has the advantage that there are several options for producing it, including use of renewable energy sources. Hydrogen, as energy carrier, can also be used for energy storage and can be easily converted to electric energy and heat. Over recent years, the necessity to research alternative energy sources has become increasingly important. [2]

Hydrogen being the simplest and the most abundantly applicable element in the universe (0.9wt%) is present everywhere. Being an energy carrier, hydrogen (a means of strong and transporting energy) is not an energy source itself, but it can only be produced from other sources of energy, such
Table 1. Basic thermodynamic data of hydrogen.

<table>
<thead>
<tr>
<th>State</th>
<th>(\Delta H^°) (KJ mol(^{-1}))</th>
<th>(\Delta G^°) (KJ mol(^{-1}))</th>
<th>(\Delta S^°) (JK mol(^{-1}))</th>
<th>Cp (JK mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas H</td>
<td>218</td>
<td>203</td>
<td>115</td>
<td>21</td>
</tr>
<tr>
<td>(H_2)</td>
<td>0</td>
<td>0</td>
<td>131</td>
<td>29</td>
</tr>
</tbody>
</table>

Table 2. Selected physical properties of hydrogen.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>2.016</td>
<td>mol</td>
</tr>
<tr>
<td>Melting point</td>
<td>13.96</td>
<td>K</td>
</tr>
<tr>
<td>Boiling point (at 1atm)</td>
<td>14</td>
<td>K</td>
</tr>
<tr>
<td>Density solid at 4.2 K</td>
<td>0.089</td>
<td>g(^{3})</td>
</tr>
<tr>
<td>Density liquid at 20.4 K</td>
<td>0.071</td>
<td>g cm(^{-3})</td>
</tr>
<tr>
<td>Gas density (at 0 °C and 1atm)</td>
<td>0.09</td>
<td>g L(^{-1})</td>
</tr>
<tr>
<td>Gas thermal conductivity (at 25 °C)</td>
<td>0.00044</td>
<td>Cal cm s(^{-1}) cm(^{-2}) °C(^{-1})</td>
</tr>
<tr>
<td>Gas viscosity (at 25 °C and 1atm)</td>
<td>0.0089</td>
<td>Centipoise</td>
</tr>
<tr>
<td>Gross heat of combustion (at 25 °C and 1atm)</td>
<td>265.0339</td>
<td>KJ g(^{-1}) mol(^{-1})</td>
</tr>
<tr>
<td>Net heat of combustion (at 25 °C and 1atm)</td>
<td>241.9292</td>
<td>KJ g(^{-1}) mol(^{-1})</td>
</tr>
<tr>
<td>Autoignition temperature (at 25 °C and 1atm)</td>
<td>858</td>
<td>K</td>
</tr>
<tr>
<td>Flammability limit in oxygen</td>
<td>4 - 94</td>
<td>%</td>
</tr>
<tr>
<td>Flammability limit in air</td>
<td>4 - 74</td>
<td>%</td>
</tr>
</tbody>
</table>

as fossil fuels (natural gas, coal, and petroleum), or renewable sources (biomass, wind, solar, and geothermal) by means of several different energy conversion processes.[3-6]

Hydrogen is nontoxic, colorless, and tasteless, causing no problems when taken breath with ambient air. It is environment friendly and nonpollutant; releasing hydrogen has no effect on atmosphere (no greenhouse gas effect) or water (under normal atmospheric conditions, hydrogen is a gas with a very low solubility in water of 0.01911 dm\(^3\) at 25 °C, 0.1 MPa). Hydrogen is highly flammable; therefore proper ventilation and sensing must be assured when hydrogen diffuses into nonflammable concentrations. During combustion, only water vapor is produced.

Thermodynamic data of hydrogen at 25.15 °C and 0.1 MPa are presented in Table 1. [7] Selected
physical properties of hydrogen based on Van Nostrand are as following Table 2. [8]

2.2 Hydride Compounds

Hydrogen as a gas has only a density of 0.09 g L⁻¹ under standard temperature and pressure conditions. When liquid state, hydrogen exhibits a modest density of 70 g L⁻¹. But the extremely low condensation temperature of 20 K makes the energy consumption for liquidation substantial. (Table 2) Alternatively, hydrogen can be stored as a compressed gas under ~35 MPa at room temperature with 15 g H₂ per L. However, such an approach may not be cost effectively because the resulting product will have a low energy density, and there are some safety issues. Therefore, considerable

<table>
<thead>
<tr>
<th>Substance</th>
<th>Reaction (ambient temperature)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Humid air</td>
</tr>
<tr>
<td><strong>Chemical Hydride</strong></td>
<td></td>
</tr>
<tr>
<td>Lithium hydride [LiH]</td>
<td>Can ignite</td>
</tr>
<tr>
<td>Sodium hydride [NaH]</td>
<td>Ignites</td>
</tr>
<tr>
<td>Potassium hydride [KH]</td>
<td>Inflames</td>
</tr>
<tr>
<td>Rubidium hydride [RbH]</td>
<td>Inflames</td>
</tr>
<tr>
<td>Cesium hydride [CsH]</td>
<td>Inflames</td>
</tr>
<tr>
<td>Magnesium hydride [MgH₃]</td>
<td>Known to ignite</td>
</tr>
<tr>
<td>Calcium hydride [CaH₂]</td>
<td>Moderate fast</td>
</tr>
<tr>
<td>Barium hydride [BaH₂]</td>
<td>Rapid</td>
</tr>
<tr>
<td>Aluminum hydride [AlH₃]</td>
<td>Slow</td>
</tr>
<tr>
<td><strong>Complex Hydride</strong></td>
<td></td>
</tr>
<tr>
<td>Lithium borohydride [LiBH₄]</td>
<td>Rapid</td>
</tr>
<tr>
<td>Lithium aluminum hydride [LiAlH₄]</td>
<td>Rapid</td>
</tr>
<tr>
<td>Sodium borohydride [NaBH₄]</td>
<td>Slow</td>
</tr>
<tr>
<td>Sodium aluminum hydride [NaAlH₄]</td>
<td>Rapid</td>
</tr>
<tr>
<td>Potassium borohydride [K BH₄]</td>
<td>Very slow</td>
</tr>
<tr>
<td>Magnesium borohydride [Mg(BH₄)₂]</td>
<td>Very slow</td>
</tr>
<tr>
<td>Magnesium aluminum hydride [Mg(AlH₄)₂]</td>
<td>Vigorous</td>
</tr>
<tr>
<td>Beryllium borohydride [Be(BH₄)₂]</td>
<td>Explosive</td>
</tr>
<tr>
<td>Aluminum borohydride [Al(BH₄)₃]</td>
<td>Explosive</td>
</tr>
</tbody>
</table>
effort has been directed toward materials-based hydrogen storage methods. There are typically two types of mechanisms for hydrogen storage: physisorption and chemisorption. In the first category, hydrogen binds to the storage materials that have a large surface area via van der Waals interactions. Examples in this category include carbon-based nanostructures and metal–organic frameworks (MOFs). [9] On the other hand, the atomic binding of hydrogen to the storage materials through covalent, ionic or metallic bonds constitutes the chemisorptive hydrogen storage. This category typically involves hydrogen-rich materials, often referred to as hydrides. Depending on the identity of the non-hydrogen moiety of the materials, hydrides can be further classified as (1) simple hydrides or (2) complex hydrides. [10-15] Simple hydrides react with water to form hydrogen according to the literature. [16] These hydrides and the reactivity with water are summarized in Table 3. [17]

Simple hydride to generate hydrogen was developed by the U.S. Army Mobility Equipment Research and Development Command. [18] A schematic diagram of this device is shown in Fig.1. Water flows from the reservoir into the water chamber where it contacts a porous hydrophobic membrane.
membrane. Water vapor diffuses through the membrane and spontaneously reacts with the hydride to release hydrogen. The hydrogen then flows out of the reaction chamber to the anode of the fuel cell. Hydrogen production is controlled by effect of water being forced back into the water reservoir during periods of no load, when hydrogen is not being consumed at the anode. As hydrogen is consumed by the fuel cell during periods of load, the water level will self-regulate to generate only the required amount of hydrogen.

Foulkes et al. reported the reactivities of various other hydride powders for reaction with water vapor. The reactor configuration for reaction with water vapor is shown in Fig.2 and the results are summarized in Fig.3. [19] None of the hydrides reacted as completely as CaH$_2$. LiH and LiAlH$_3$ gave fairly constant hydrolysis rates up to almost 69% conversion, and gave reasonably high ultimate yields as well. The reaction products of these two hydrides were contained in the mesh cylinder as hard solid masses. The overall yield likely was limited by the inaccessibility to water vapor of unreacted hydride in the interior of the cylindrical bed. NaAlH$_4$ gave a constant hydrogen

![Fig.2 Hydride reactor for reaction with water vapor.](image_url)
Fig. 3 Hydrogen production profiles for reaction of different hydrides with water vapor using reactor in Fig. 2. System nominally at room temperature.

summarized in Fig.3. [19] None of the hydrides reacted as completely as CaH$_2$. LiH and LiAlH$_3$ gave fairly constant hydrolysis rates up to almost 69% conversion, and gave reasonably high ultimate yields as well. The reaction products of these two hydrides were contained in the mesh cylinder as hard solid masses. The overall yield likely was limited by the inaccessibility to water vapor of unreacted hydride in the interior of the cylindrical bed. NaAlH$_4$ gave a constant hydrogen production rate up to about 42% yield. However, the ultimate yield was only 49%, making its effective deliverable hydrogen storage capacity less than that of CaH$_2$. The reaction product was contained in the mesh cylinder as a semi-solid mass. LiBH$_4$ and NaBH$_4$ did not react with water vapor. There was no reaction with these materials until the hygroscopic borohydride powders effectively dissolved and flowed into the liquid water in the bottom of the reactor. The yields were very low because of increased solution pH upon reaction to form hydroxides (borohydrides are stable in alkaline solutions).

2.3 Aluminum

High-level integration like with liquid hydrocarbons within global energy is possible only in case of energy carriers based on the most widespread chemical elements in the earth’s crust or lithosphere.
In simple case the energy can be stored in the form of chemical energy of reduced inorganic substances such as hydrogen [20,21], silicon [22], aluminum [23], iron [24], magnesium [25] and others. The process of energy accumulation occurs when the substance is produced from respective oxide. The energy is then regenerated, when the substance is oxidized. Such energy carriers differ from the conventional energy storage technologies because they represent the renewable synthetic fuels. They can be stored for a long time with negligible self-discharge and easily transported to any distance like fossil fuels.

Aluminum is one of the most widespread chemical elements in the outer 16 km of the crust (about 8% by weight [26, 27]); only oxygen and silicon are more widespread, while among metals aluminum takes first place. The earth’s crust contains aluminum mainly in the form of aluminum silicates.

Hydrogen production method based on aluminum oxidation in alkaline aqueous solutions is one of the oldest and more than century-known as well. [28-30] The process of hydrogen generation in this case goes through electrochemical reaction. Overall reaction is described by following equation:

\[ 2\text{Al} + 6\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 + 3\text{H}_2 \]

The kinetics of aluminum oxidation in alkaline aqueous solution is a topic of many investigations, which have been continuing up to now. [31-37] Hydroxide ions (OH\(^-\)) in strongly alkaline solutions are able to destroy the protective oxide layer on the aluminum surface forming AlO\(_2^−\). Therefore, aluminum and its alloys are readily dissolved in the alkaline environment even at room temperature, resulting in hydrogen production. Among various alkaline compounds, sodium hydroxide (NaOH) is the most commonly encountered alkali with the following series of reactions:

\[ 2\text{Al} + 6\text{H}_2\text{O} + 2\text{NaOH} \rightarrow 2\text{NaAl(OH)}_4 + 3\text{H}_2 \quad (1) \]

\[ \text{NaAl(OH)}_4 \rightarrow \text{NaOH} + \text{Al(OH)}_3 \quad (2) \]

\[ 2\text{Al} + 6\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 + 3\text{H}_2 \quad (3) \]
The two steps, shown in the equations above, were suggested to be involved in this hydrogen generation process [38-40]. NaOH depleted for the hydrogen evolution in step (1) will be regenerated through the NaAl(OH)$_4$ decomposition in step (2). Therefore, essentially, only water is consumed during the whole process if the reaction is properly controlled. Adding steps (1) and (2) together yields the overall reaction as expressed by Eq. (3). Although it is a well-known parasitic reaction, which is undesirable in alkaline–aluminum–air batteries, this reaction indeed provides a compact source of hydrogen. So far, a number of hydrogen generation devices have been developed based on this reaction. [28, 29, 32, 41-47]

Fig.4 (a) Schematic diagram and (b) laboratory prototype for hydrogen production from aluminum.

Wang et al. proposed a safe and simple hydrogen generator based on hydrogen produced by the aluminum oxidation in NaOH aqueous solution for feeding PEM fuel cell. [48] This generator operated stably a single cell under 500mA for nearly 5h, with about 77wt% H$_2$ utilization ratio. About 38 mLmin$^{-1}$ of hydrogen rate was obtained with 25% concentration and 0.01 mLs$^{-1}$ dropping rate of NaOH solution. Schematic diagram and the laboratory setup for hydrogen generation from aluminum are shown in Fig.4.

It seems that aluminum could provide alternative source of hydrogen for onboard use. Further investigations in this chapter are ongoing.
2.4 Lithium Ion Battery

The performances of LIBs highly depend on the structure and properties of the active electrode materials and electrolytes, especially the characteristics of cathode materials. LiCoO$_2$ is the major cathode material currently, which provides an energy density of $\sim$150 Wh kg$^{-1}$. However, LiCoO$_2$ is undesirable to be applied in the field of EVs and HEVs due to the low energy density and the drawbacks of high cost and safety concern. [49] Much efforts have been made for a long time to develop cathode materials with high discharge voltage platforms and large capacities to improve the energy density of LIBs. Up to now, the most studied cathode materials include three types, poly-anion oxides, spinel-type oxides, and $\alpha$-NaFeO$_2$-type layered oxides, and the representatives are LiFePO$_4$, LiMn$_2$O$_4$, and LiNi$_x$Co$_y$Mn$_{1-x-y}$O$_2$, respectively. [50] However, the practical capacities of these materials are comparable to or only slightly higher than those of commercial LiCoO$_2$. Since the mass energy density is the product of discharge capacity and average discharge voltage, it is critical to search for materials with high discharge voltage plateaus, which can provide much more room to improve the energy density. [51]

The high-voltage cathode materials that have been reported are summarized in Table 4, most of which are based on the above three types of materials. [52] Polyanionic cathode materials have been extensively investigated since Padhi et al.’s report [78], which mainly include phosphates (such as olivine LiMPO$_4$, and monoclinic Li$_3$M$_2$(PO$_4$)$_3$) [79-82], pyrophosphates [83], fluorophosphates [84-86], borates LiMBO$_3$ [87], tavorite fluorosulphates LiMSO$_4$F [88], and orthosilicates Li$_2$MSiO$_4$ .[89] The olivine phosphates (LiMPO$_4$) exhibit moderate theoretical discharge capacity, high thermodynamic stability, and stable discharge platform. The redox potentials are 3.5, 4.1, 4.8, and 5.1 V (vs. Li/Li$^+$) when M = Fe, Mn, Co, and Ni, respectively. [54] LiFePO$_4$ is particularly remarkable due to its good cyclic performance, abundant raw materials, non-toxicity, etc. However, the lower discharge plateau leads to lower energy density compared with LiCoO$_2$. Due to the low
The capacities are based on the extraction of one Li\(^{+}\) per formula, and the practical capacity may exceed the data.

### Table 4. Electrochemical data of high-voltage cathode materials

<table>
<thead>
<tr>
<th>Substance</th>
<th>Average discharge potential [ V \text{ (vs. Li }/\text{ Li}^{+}\text{)} ]</th>
<th>Redox couple(^a)</th>
<th>Theoretical capacity [ \text{mAh g}^{-1}]</th>
<th>Potential range [ V \text{ (vs. Li }/\text{ Li}^{+}\text{)} ]</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoPO(_4)</td>
<td>4.8</td>
<td>Co(^{2+/3+})</td>
<td>167</td>
<td>3.0 – 5.1</td>
<td>[53]</td>
</tr>
<tr>
<td>LiNiPO(_4)</td>
<td>−5.1</td>
<td>Ni(^{2+/3+})</td>
<td>167</td>
<td>3.0 – 5.1</td>
<td>[54]</td>
</tr>
<tr>
<td>Li(_3)V(_2)(PO(_4))(_3)</td>
<td>3.8</td>
<td>V(^{2+/4+/5+})</td>
<td>197</td>
<td>3.0 – 4.8</td>
<td>[55]</td>
</tr>
<tr>
<td>Li(_2)CoPO(_4)</td>
<td>4.9</td>
<td>Co(^{2+/3+})</td>
<td>109(^b)</td>
<td>2.0 – 5.5</td>
<td>[56]</td>
</tr>
<tr>
<td>Li(_2)MnPO(_4)</td>
<td>4.45</td>
<td>Mn(^{2+/3+})</td>
<td>110(^b)</td>
<td>2.0 – 4.7</td>
<td>[57]</td>
</tr>
<tr>
<td>Li(_2)CoPO(_4)F</td>
<td>−4.9</td>
<td>Co(^{2+/3+})</td>
<td>143(^b)</td>
<td>3.0 – 5.5</td>
<td>[58,59]</td>
</tr>
<tr>
<td>Li(_2)NiPO(_4)F</td>
<td>−5.1</td>
<td>Ni(^{2+/3+})</td>
<td>143(^b)</td>
<td>3.0 – 5.5</td>
<td>[60]</td>
</tr>
<tr>
<td>LiCoSO(_4)F</td>
<td>4.7–4.9(^c)</td>
<td>Co(^{2+/3+})</td>
<td>149</td>
<td>–</td>
<td>[61–63]</td>
</tr>
<tr>
<td>LiNiSO(_4)</td>
<td>5.2–5.4(^c)</td>
<td>Ni(^{2+/3+})</td>
<td>149</td>
<td>–</td>
<td>[61–63]</td>
</tr>
<tr>
<td>LiCuSO(_4)F</td>
<td>5.1(^c)</td>
<td>Cu(^{2+/3+})</td>
<td>145</td>
<td>–</td>
<td>[62]</td>
</tr>
<tr>
<td>LiCoOSO(_4)F</td>
<td>5.1(^c)</td>
<td>Co(^{3+/4+})</td>
<td>152</td>
<td>–</td>
<td>[62]</td>
</tr>
<tr>
<td>LiNiSO(_4)</td>
<td>5.0(^c)</td>
<td>Ni(^{3+/4+})</td>
<td>152</td>
<td>–</td>
<td>[62]</td>
</tr>
<tr>
<td>Li(_3)NiSiO(_4)</td>
<td>4.8(^d)</td>
<td>Ni(^{2+/3+})</td>
<td>163(^b)</td>
<td>–</td>
<td>[64]</td>
</tr>
<tr>
<td>Li(_2)O(<em>x)Mn(</em>{1.5})O(_4)</td>
<td>4.7</td>
<td>Mn(^{2+/3+/4+})</td>
<td>147</td>
<td>3.5 – 4.9</td>
<td>[65]</td>
</tr>
<tr>
<td>LiCr(<em>x)Mn(</em>{1+y})O(_4) (0.5&lt;y&lt;1)</td>
<td>−4.5–4.8</td>
<td>Cr(^{3+/4+}), Mn(^{3+/4+})</td>
<td>−151</td>
<td>3.4 – 5.4</td>
<td>[66,67]</td>
</tr>
<tr>
<td>LiCo(<em>x)Mn(</em>{1+y})O(_4) (0.5&lt;y&lt;1)</td>
<td>−4.5–4.9</td>
<td>Co(^{3+/4+}), Mn(^{3+/4+})</td>
<td>−145</td>
<td>3.0 – 5.3</td>
<td>[68,70]</td>
</tr>
<tr>
<td>LiFe(_x)O(<em>x)Mn(</em>{1+y})O(_3)</td>
<td>4.5</td>
<td>Fe(^{3+/4+}), Mn(^{3+/4+})</td>
<td>148</td>
<td>3.0 – 5.3</td>
<td>[71,72]</td>
</tr>
<tr>
<td>LiCu(_x)O(<em>x)Mn(</em>{1+y})O(_3)</td>
<td>−4.3</td>
<td>Cu(^{2+/3+}), Mn(^{3+/4+})</td>
<td>145</td>
<td>3.3 – 5.1</td>
<td>[73–75]</td>
</tr>
<tr>
<td>xLi(<em>2)Mn(</em>{1+y})O(_3) (1−x)LiMeO(_2) (0&lt;x&lt;1, Me = Ni, Co, Mn)</td>
<td>3.5</td>
<td>Ni(^{2+/3+}), Co(^{3+/4+}), Mn(^{3+/4+})</td>
<td>~134(^d)</td>
<td>2.0 – 4.8</td>
<td>[76]</td>
</tr>
<tr>
<td>LiNiVO(_4)</td>
<td>4.8</td>
<td>Ni(^{2+/3+})</td>
<td>148</td>
<td>3.0 – 5.3</td>
<td>[77]</td>
</tr>
</tbody>
</table>

\(^a\) \(M^{x+/y+/z+}\) means three couples: \(M^{x+/y+}, M^{x+/z+}, M^{x+/z+}\).

\(^b\) The capacities are based on the extraction of one Li\(^{+}\) per formula.

\(^c\) The data are obtained by theoretical estimation, and no experimental data are available.

\(^d\) The capacity is based on the extraction of one Li\(^{+}\) per formula, and the practical capacity may exceed the data.

The capacity is based on the extraction of one Li\(^{+}\) per formula, and the practical capacity may exceed the data. The data are obtained by theoretical estimation, and no experimental data are available. The capacity is based on the extraction of one Li\(^{+}\) per formula, and the practical capacity may exceed the data.

The introduction of V\(^{3+/4+/5+}\), Co\(^{2+/3+}\) and Ni\(^{2+/3+}\) couples (Li\(_3\)V\(_2\)(PO\(_4\))\(_3\), LiCoPO\(_4\), Li\(_2\)CoPO\(_4\)F, LiNiPO\(_4\), etc.) could increase the discharge plateaus and the energy density noticeably. For spinel oxide LiMn\(_2\)O\(_4\), the discharge plateau could also be improved by replacing Mn partly with other transition metal ions with high potential couples (Ni\(^{2+/3+/4+}\), Cr\(^{3+/4+}\), Co\(^{3+/4+}\), etc.). The discharge potentials of layered oxides LiNi\(_x\)Co\(_{3−x}\)Mn\(_{1−y}\)O\(_2\) are unlikely to be improved remarkably due to the restriction of Ni\(^{2+/3+/4+}\) and Co\(^{3+/4+}\) couples. However, the composites of LiNi\(_x\)Co\(_y\)Mn\(_{1−x−y}\)O\(_2\) and Li\(_2\)MnO\(_3\) exhibit super large capacities (>300 mAh g\(^{-1}\)) and high energy densities under high charge/discharge cutoff voltages (above 4.5 V) [76], which are also the candidate cathode materials for high voltage LIBs.
2.5 Heterogeneous Oxidation Catalyst

Selective oxidation reactions play a pivotal role in the current chemical industry. Oxidation is the second largest process after polymerization and contributes B30% of total production in the chemical industry. Many key chemicals and intermediates such as alcohols, epoxides, aldehydes, ketones and organic acids are produced via selective oxidation catalysis.

The reason for this is that oxidation is the tool for the production of huge quantities of intermediates and monomers for the polymer industry (Table 5). The impact of these productions on the environment might have been much greater than it is if considerable effort had not been spent on the continuous improvement of the technologies used for the production of these chemicals, including the replacement of toxic or dangerous reactants, better heat recovery and energy integration in the plant, recovery of waste streams and abatement of tail emissions, and downstream use of by-products. In the chemical industry, oxidation is one of the technologies with the greatest potential for improvement, and this has led to a series of better processes in recent years. All improvements in catalyst, reaction, and process technologies have moved in the direction of an improved sustainability, and have been widely documented in the books and papers published in recent years. Although the developments were driven by economics, this has also led to more sustainable processes. However, some processes still co-produce large amounts of waste, or operate under conditions leading to non-optimal selectivity to the desired compound.

For the above reason, selective oxidation catalysis is also the key to establishing green and sustainable chemical processes. Take selective oxidation of hydrocarbons as an example. On one hand, the selectivity in the current chemical industry has to be further raised to decrease the formation of non-selective products, particularly CO2. This requires further optimization of the catalyst and the process employed in the current chemical industry. On the other hand, there is a strong incentive to develop new oxidation processes that satisfy the principles of green
**Table 5. Organic base chemicals produced by means of oxidation**

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Capacity [Mta⁻¹]</th>
<th>Oxidant</th>
<th>Air</th>
<th>O₂</th>
<th>HNO₃</th>
<th>Cl₂</th>
<th>ROOH</th>
<th>H₂O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terephthalic acid</td>
<td>44</td>
<td>○</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>19</td>
<td>○</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethene oxide</td>
<td>18</td>
<td>○</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>18</td>
<td>○</td>
<td>○</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propene oxide</td>
<td>8</td>
<td>○</td>
<td></td>
<td>○</td>
<td></td>
<td></td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>6</td>
<td>○</td>
<td>○</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vinyl acetate</td>
<td>6</td>
<td>○</td>
<td></td>
<td>○</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>6</td>
<td>○</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Styrene</td>
<td>5</td>
<td>○</td>
<td></td>
<td>○</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol / acetone</td>
<td>5</td>
<td>○</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phthalic anhydride</td>
<td>5</td>
<td>○</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Acrylic acid</td>
<td>5</td>
<td>○</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MTBE[a]</td>
<td>4</td>
<td>○</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adipic acid</td>
<td>3</td>
<td>○</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maleic anhydride</td>
<td>2</td>
<td>○</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen cyanide</td>
<td>2</td>
<td>○</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[a] MTBE : methyl-tert-butyl ether

chemistry.[135,136] In particular, it is highly desirable to develop new catalytic oxidation processes to replace the current energetically inefficient and/or environmentally unfriendly multi-step reactions.

### 2.6 Heterogeneous NOx Reduction Catalyst

The selective catalytic reduction (SCR) of NOx in mobile exhaust streams is an effective and promising technology. In the SCR process, NOx’s are converted into N₂ using a sacrificial reducing agent over a catalyst surface.[137-145] SCR technologies are subcategorized on the basis of the reducing agent used to achieve the same chemical reaction, that is, the breakdown of NOx into N₂.

Two major SCR technologies that have reached or are reaching commercialization are based on hydrocarbon-SCR (HC-SCR) and urea-SCR (also referred to as ammonia-SCR). Perhaps less
popular has been SCR technologies using CO or H\textsubscript{2} as a reducing agent, [141] although the latter has been found necessary to enable low-temperature activity in HC-SCR. [146]

The lean-burn engine is actually the most attractive solution combining low consumption and low CO\textsubscript{2} emission, recognized for its greenhouse gas behavior. However, the current three-way technology used near stoichiometric conditions is unable to meet the regulations in Europe, United States, and Japan.

A high-throughput approach, aided by multiobjective design of experiments based on a genetic algorithm, was reported to optimize the combinations and concentrations of a noble metal free catalyst active in the selective reduction of NO with C\textsubscript{3}H\textsubscript{6}. [147] Using adequate variation operators and constraint handling techniques the investigation checked a multi objective approach to test the ability not only to find the best catalyst formulation but also to find multiple best catalysts with respect to several goals. One of the important questions addressed by these studies was whether binary combinations can provide enough active catalysts or the use of multicomponent systems is required. The experimental design was composed of 11 elements in different combinations and concentrations that can be classified into three groups: (i) elements acting as support, (ii) the main elements with likely a major contribution to the catalytic efficiency, and (iii) elements acting as promoter. Al was chosen as element for the support, Cu, Ni, Co, Fe, Mn, La, Ce, and Sm were chosen as active elements, and K and Sr were chosen as promoters. The best noble metal free catalysts found by this method are combinations of Cu or Ni with Al. Other active catalysts at low temperature included Co and Fe. Several catalysts based on transition metals (Cu, Co, Fe) and different supports (ZSM-5, activated carbon, Al\textsubscript{2}O\textsubscript{3}) have been tested in the selective catalytic reduction of NOx with propene in the presence of an excess of oxygen, simulating lean-burn conditions from diesel engines. [148] The efficiency order with respect to the metal was Cu \sim Fe > Co with ZSM-5-based catalysts having superior behavior over Al\textsubscript{2}O\textsubscript{3}. Various kinds of metal oxide
supported Cu catalysts have been thoroughly investigated in the HC-SCR such as Cu/SiO$_2$.[149] Cu/Al$_2$O$_3$,[150] and Cu/ZrO$_2$. [151] However, the deactivating effect of SO$_2$ on the selective catalytic reduction over CuO/Al$_2$O$_3$ catalysts has been reported and assigned to the formation of ammonium and copper sulfates.[152,153]

Despite a huge number of investigations at the laboratory scale for improving the thermal stability of noble metal free catalysts and their sulfur tolerance, it is obvious that no practical solution has arisen yet able to compete efficiently with noble metals except urea-SCR catalyst for heavy duty vehicles.

3 Summary

Chapter 1 presents the hydrogen generation method which gives moderate production rate through the control of surface area, completely different from conventional methods. The obtained materials are analyzed to clarify their hydrogen generation abilities.

In Chapter 2, the 5V cathode material LiNi$_{0.5}$Mn$_{1.5}$O$_4$ was synthetized by a simple wet chemical reaction using acetates as precursor’s materials. Cathode active materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and Inductively Coupled Plasma (ICP).

Chapter 3 presents the novel preparation methods of a high-valent Mn oxide species on hydrotalcites and Copper (II) chloride complexes within pores of zeolite X. These materials found to act as a heterogeneous catalyst for the oxidation of a variety of alcohols and enamines in the presence of molecular oxygen without leaching of the active species.

Chapter 4 describes about the preparation method of high dispersed copper species for the reduction of NOx.
4 References


Chapter 1

Application to hydrogen generating materials for fuel cell

1.1 Modification of Calcium Hydride as Solid Hydrogen Source for Fuel Cell System

1.1.1 Introduction

Hydrogen is known as an ultimate clean energy source that does not generate carbon dioxide after combustion. In addition, it can be used as a power source for fuel cells that directly extract the energy change of the chemical reaction as the electric power. It is well known that organic hydrides, such as a methyl cyclohexane, are indispensable in the development of hydrogen carriers for hydrogen storage systems in large-scale facilities and FCV. In addition, by installing an internal fuel oil reformer, the stationary ENE-FARM takes advantage of the existing infrastructure, such as city gas or LP gas, to extract hydrogen gas.

However, the use of hydrogen is not limited to examples mentioned above. For example, a fuel cell can be used as an alternative generation source to a gasoline or diesel engine generator during disasters; a fuel cell is quiet and can be utilized in a room because its by-product is only water. Moreover, when power generation is required in a mountainous area, where infrastructure is not in place, the fuel cell, because of its portability, would be very effective if it can be used as an alternative to a lead-acid battery. In this regard, the construction of an on-demand-type portable hydrogen generation system is one of the most important topics in the utilization of hydrogen technologies. Such a portable hydrogen generation system would need to have a small weight load and generate only the required amount of hydrogen when and where required; a hydrogen cylinder and a hydrogen storage alloy, for example, would meet these requirements.

In this chapter, metal hydrates were focused, which generate hydrogen easily when in contact
with water under ambient temperature and pressure. As shown in Figure 1, the hydrates were roughly classified into two categories: simple hydrides and complex hydrides. The numerical values on the vertical axis of Figure 1 indicate the hydrogen content of each hydride (wt %). [1, 2] To search for metal hydrates with potential as solid hydrogen sources, the author screened the compounds based on the results (I) to (VI), along with the hydrogen contents (wt%) of each compound: (I) among simple hydrides, lithium hydride (LiH), sodium hydride (NaH), and potassium hydride (KH) have high reactivities with water and have the risk of spontaneous combustion [3,4]; (II) aluminum hydride compounds also react violently with water in the same manner as in (I). Particularly, the reactivity of lithium aluminum hydride (LiAlH₄) exceeds that of the compounds in (I), and therefore it must be completely isolated from moisture in air when it is not in use [4,5]; (III) Li-based compounds are problematic because of their costs; (IV) magnesium hydride (MgH₂) forms an oxide film (passive layer) of Mg(OH)₂ on its surface. Thus, a secondary procedure, such as temperature regulation, pH control, or cracking using a ball mill, is required to remove the oxide film (passive layer) to generate hydrogen [6,7]; (V) aluminum hydride (AlH₃) has a risk of spontaneous combustion immediately after synthesis. It requires time to form the oxide film (passive layer) of Al₂O₃ on its surface; moreover, heating is necessary to generate hydrogen [8-10]; and (VI) borohydride compounds are very stable in the presence of water. Controlling those pH and adding a metal catalyst are necessary to extract hydrogen gas efficiently. [11-13] As a result of comprehensive consideration of safety, convenience, and costs, calcium hydride (CaH₂) was selected as the optimal solid hydrogen source.
Fig. 1 Hydrogen content of each hydrogenated inorganic compound
1.1.2 Experimental

Modification of Calcium hydride

After stirring the mixture of 0.8687 g of epoxy resin and 1.2 g of calcium hydride, by addition of 0.069 g of dicyandiamide type hardener and 0.0123 g of hardening accelerator [2,4,6-Tris(dimethylaminomethyl)phenol], the mixture was further stirred. Finally, this viscous material was shaped by pressing about 10 MPa under 125 °C for 60 minutes. The thickness of materials obtained was 1.8 mm and the content of calcium was 55 wt%. [14]

1.1.3 Results and Discussion

Solid hydrogen source

Calcium hydride generates hydrogen (gas) and calcium hydroxide (solid) by reacting with water, as shown in equation (1):

\[ \text{CaH}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{Ca(OH)}_2 \]  (1)

Calcium hydride has long been used as a dehydrating material in organic synthesis reactions because it can be separated easily from the liquid phase by decantation. Its degree of risk is lower than that of alkali-metal-based hydrides, but it also emits hydrogen immediately on reaction with water. [4] To utilize this material in powder form and provide stable supplies of hydrogen to fuel cells, an equipment group similar to the cylinders of a pressure-resistance reactor and a pressure regulating valve is required. Accordingly, modification of CaH₂ was attempted for the supply of hydrogen to fuel cells at a constant flow rate without using the equipment above mentioned. In this new method, thermoset resin and calcium hydride are mixed, and calcium hydride powders are dispersed and solidified within the resin (Figure 2). Figure 3-1 and 3-2 shows photographs before and after sealing. The piece of sheet (3 g) shown in Figure 3-2 can provide 4.5 L of hydrogen, which can completely
Fig. 2 Resin sealing of calcium hydride

CaH₂ [powder] + Thermoset resin [liquid + powder] → Resin sealing body [solid]

Fig. 3.1 Calcium hydride (powder)

Fig. 3.2 Calcium hydride (resin molding)
charge a single standard smartphone. Because the sheet can block the moisture in air by aluminum-laminate processing to prevent the degradation of the fuel, it can be preserved for a long period of time (>20 years) without the loss of energy. This feature cannot be realized with lithium-ion secondary batteries or alkaline batteries, making calcium hydride an effective material as a power source for disaster countermeasures. Figure 4 shows the result of tracking the generation of hydrogen by contacting a material treated by resin sealing with water. This material was successful in prolonging the time of hydrogen generation up to 120 minutes. In addition, the rate of hydrogen generation could be controlled by changing the mixing ratio of resin and calcium hydride. Figure 5 shows the result of examining the combination of different resins and solid hydrogen sources. Regardless of the resin type, calcium hydride produced hydrogen in a more stable and efficient manner than sodium borohydride (NaBH₄) solid hydrogen sources. This result is believed to stem from the continuous holes formed in the calcium hydride materials that allow water to be supplied completely to every corner. Cracking also occurs in the resin portion when hydrogen flows rate is high (high output); this results in the expansion of the material on hydrogen generation, which secures water supply lines. These phenomena may explain why the hydrogen yields do not decline, even when sealed with thermoset resins. Because the reaction between calcium hydride and water is exothermic, the resin is able to flow during the reaction in the molding with a thermoplastic resin. Consequently, the contact of calcium hydride with water is inhibited, and the reaction rate decreases (Figure 5).

**Hydrogen flow control**

Two methods can be used to extract hydrogen using a solid hydrogen source treated by resin molding: the immersion method, in which an amount of water sufficient to completely submerge the material is added at once; and the dropping method, in which one drop of water is added at a time. The control over the amount of generated hydrogen by the dropping method is effective when
Fig. 4 Examination of the mixing ratio of thermosetting and calcium hydride
Fig. 5 Examination of hydrogen generation with different combinations of solid hydrogen sources and resins
considering the on-off function of an electric power supply. Figure 6 shows the schematic of an internal pressure control device designed to control the amount of power generation. Because hydrogen generated by the dropping method is consumed in a fuel cell when an external power source is turned on, water is continuously supplied to the solid hydrogen source, and hydrogen is thus continued to be fed into the fuel cell. Meanwhile, when the external power supply is turned off, there is no consumption of hydrogen, and the internal pressure rises automatically. When the internal pressure rises, the water flow, as shown in Figure 6, changes to move in the direction opposite to the arrow. The amount of water supplied to the hydrogen-generating section then becomes zero, and it is possible to stop the generation of hydrogen. [15] Hydrogen generation control system was successfully built, which does not rely on the external power supply in the abovementioned manner.

**Thin fuel cell**

Following the resin encapsulation processing of solid hydrogen sources and the control of the amount of hydrogen generation by the internal pressure control, a thin fuel cell was developed to downsize the fuel cells to minimize weight during their operation at normal temperatures. As shown in Figure 7, the downsizing for one cell of the fuel cells to the size of an adult’s little finger was attempted. The cross-sectional view of the internal structure is shown in Figure 8. The fuel cell type is a polymer electrolyte (PEFC) in which the major components (a cathode, a solid polymer membrane, and an anode) are sufficiently close to increase the power-generation efficiency. [16] While PEFCs are generally bolted, the normal temperature operation of the PEFC in this study was enabled by developing it using the insert molding of resins. Although insert molding is not possible in conventional large cells because of an insufficient rise in pressure, small cells are able to support this type of technique.

*Types and features of the Solid Hydrogen Source Fuel Cell System*

The developments were carried out for the products with the three core technologies
Fig. 6. Hydrogen flow rate control system
Fig. 7. Thin Fuel cells

Fig. 8. Schematic cross section diagram of thin fuel cell
abovementioned as follows.

Small-Type fuel cell (Rated voltage: 5 V$_{DC}$; amount of power generation: 5 Whr)

This is a small fuel cell of the card-case type (Figure 9). Hydrogen is generated to meet the requirement of fully charging (5 Whr) a standard smartphone with a sheet of less than 3 cc in volume (Figure 5-2) and water. The small-type fuel cell contains four thin cells (Figure 7). Its intended use is in various types of small-size and light-weight portable equipment and in general-purpose multipower supplies.

High-output type fuel cell (Rated voltage: 12 or 24 V$_{DC}$; amount of power generation: 200 Whr)

This is a high-output power supply of a few-hundred W classes (Figure 10) with a weight of 6–7 kg. The high-output cell can be used in a room because it produces only water, not carbon dioxide or other harmful gases, such as those emitted by gasoline generators. It is also quiet with no vibration and can be used in emergencies, as well as in campers and pleasure boats.

Hybrid high-output type fuel cell (Multioutput 5 V, USB/2-necked, AC 100 V)

The hybrid high-power fuel cell unit contains a secondary battery (LiB; Figure 11). Its hydrogen supply portion has a mechanism to set solid hydrogen source cans as cassette stoves (Figure 12), making it possible to output 200 Whr per canister. The unit canister run a 32-inch TV set for 3 hours and a 50-W equivalent PC for 4 hours. Further development is ongoing to establish the durability, safety, and convenience of these products, aiming to introduce them into markets as soon as possible after verification tests.
Fig. 9 Small-Type fuel cell

Fig. 10 High-output type fuel cell
Fig. 11 Hybrid high output type fuel cell. (a) outer view and (b) system configuration.

Fig. 12. Solid hydrogen-source canister.
1.1.4 Conclusion

New scheme for preparing the inorganic-organic hybrid type hydrogen generation material, which is achieved by the mixing of calcium hydride and epoxy resin, was proposed. This material was enabled to generate hydrogen moderately. As a result of applying this hydrogen source to fuel cell, various types of outputs generator could be designed.

1.1.5 References


Sources, **85**, 186 (2000)


1.2 Hydrogen Generation by Aluminum Powder Corrosion in Calcium Hydroxide Solutions

1.2.1 Introduction

Hydrogen is one of the important energy resources that can be consumed in a fuel cell, converting chemical energy into electrical energy with a high performance. Fuel cells, operating with hydrogen or hydrogen-rich fuels, have the potential to become major factors in catalyzing the transition to a future sustainable energy system with low CO₂ emissions.[1] In general, hydrogen gas is mainly produced in large quantities by steam reforming of hydrocarbons, such as methane. The produced gas should be compressed at 200 bar in a high-pressure tank for the storage. Another storage method for the hydrogen gas is to use the chemical reaction between water and metal hydrides, including lithium hydride (LiH), sodium hydride (NaH), lithium tetrahydridoborate (LiBH₄), and sodium tetrahydridoborate (NaBH₄). [2] Almost all hydrides shown above are stable in dry or ambient air, however, when water eventually diffuses into the hydride, the hydration reaction accelerates and it will be out of control because these reactions are highly exothermic and potentially dangerous. Therefore, the reaction at which water is combined with the chemical hydride should be precisely controlled to avoid these runaway reactions and potential explosion. Another possible method for the hydrogen gas generation is the procedure based on a corrosion of base metal such as aluminum in solutions. Hydrogen production from aluminum can provide an alternative means to produce pure hydrogen for feeding to a micro-fuel cell. The basic possible aluminum oxidation reactions in water are the following:

\[
\begin{align*}
\text{Al} + 3\text{H}_2\text{O} & \rightarrow \text{Al(OH)}_3 + 3/2\text{H}_2 \quad (1) \\
\text{Al} + 2\text{H}_2\text{O} & \rightarrow \text{AlOOH} + 3/2\text{H}_2 \quad (2) \\
\text{Al} + 3/2\text{H}_2\text{O} & \rightarrow 1/2\text{Al}_2\text{O}_3 + 3/2\text{H}_2 \quad (3)
\end{align*}
\]

All the reactions are accompanied by the release of hydrogen and solid byproducts such as bayerite.
[Al(OH)₃], boehmite [AlO(OH)], and aluminum oxide [Al₂O₃]. The advantages of using aluminum powder for the hydrogen generation exist in cost effective, high efficiency, pure hydrogen generation with high humidity, and simple changeability. [3] The reactions shown above are thermodynamically favorable; however, the presence of a passive layer containing oxides at the surface prevents the reaction between water and aluminum. Therefore, the hydration reaction of pure aluminum cannot proceed completely in water without any additives. Many reports claimed that sodium hydroxide acts as a catalyst to proceed the hydrogenating reaction in the following reaction:

\[
\text{Al} + 3\text{H}_2\text{O} + \text{NaOH} \rightarrow \text{NaAl(OH)}_4 + \text{3/2H}_2 \quad (4)
\]

\[
\text{NaAl(OH)}_4 \rightarrow \text{NaOH} + \text{Al(OH)}_3 \quad (5)
\]

The main disadvantage using NaOH solutions was that the employment of strong corrosive agent is harmful to handle and difficulty of reaction control: the strong base tends to initiate the runaway reaction. Soler et al. reported the hydrogen production curve from the hydrolysis reaction of pure aluminum or various aluminum alloys with different additives. [4, 5] They concluded that the base, its concentration, and temperature affected the hydrogen production rate. In order to apply the aluminum corrosion process into the source of hydrogen for fuel cell applications, it needs to clarify the mechanism of corrosion. In addition, the controllable hydrogen gas release, especially, the moderate evolution of the gas is also important for the wide application of fuel cells.

Here, the author demonstrated the control of hydrogen gas release in calcium hydroxide (Ca(OH)₂) solutions and analyzed the corrosion mechanism of pure aluminum powder. Calcium hydroxide was selected as a base to ignite the corrosion reactions with a safer pH even at saturation level (pH = 12.6) and easy to control not only the amount of hydrogen but also the speed of hydrogen release. The detailed investigation of residues using various surface analysis methods revealed the corrosion mechanism in the Ca(OH)₂ solutions.
1.2.2 Experimental

Raw materials used in the present work were mixture of aluminum powder (>99.99%, \(\phi = \sim 40\) \(\mu\)m, Kojundo Chemical) and calcium hydroxide, \(\text{Ca(OH)}_2\)(>95.0%, Nacalai Tesque). The \(\text{Ca(OH)}_2\) powder is added to remove the surface oxide and ignite hydration reaction of aluminum powder. The weight ratio (wt.%) of the sample mixture, \(\text{Al}/\text{Ca(OH)}_2\), was set to 80/20(Al80 Ca20), 70/30(Al70 Ca30), and 50/50(Al50 Ca50), respectively. The reactants were prepared via mixing in the mortar, and each reactant of 18 g in weight was set in the glass pot of 500 mL. Fig. 1 indicates a schematic illustration of the measurement system of the hydrogen gas generation. A distilled water of 200 mL in volume was poured into the pot and hydration reaction was initiated inside. The sample mixture was stirred using a magnetic stirrer to prevent the solidification of the product and promote the hydration reaction. Each concentration of \(\text{Ca(OH)}_2\) solution of Al80 Ca20, Al70 Ca30, and Al50 Ca50 is calculated to be 0.25, 0.37, and 0.60 mol/L, respectively. The temperature change of the solutions was monitored using K-type thermocouple. The released gas during the reaction flew through a glass tube with \(\sim 8\) mm diameter and bubbled into the water through a glass wool. The evolution rate of hydrogen gas was monitored using a flow meter and was converted into the total volume (mL) of the gas. The component of the discharged gas was analyzed using gas chromatograph (GC-2014, Shimadzu Corporation, Japan). The author used high-purity argon gas (99.99%) and SHINCARBON ST 50-80 as a carrier gas and a column in the analysis.

Residual mixture was filtered through a fine filter paper and dried for 24 h at 80 °C inside an oven. The dried mixture was ground to a fine powder using a mortar. X-ray diffraction (XRD) pat-terns of the sample powder were recorded on X-ray diffractometer (RINT2500, Rigaku, Japan) with CuK\(\alpha\) radiation for identification of their crystal structure. The microstructure of the mixture was observed using field-emission type secondary electron microscope (FE-SEM, JEOL, JSM6705F). The atomic distribution at the crystal was identified using energy dispersive X-ray spectroscopy (EDX) that
Fig.1 Schematic illustrations of measurement system of hydrogen gas release via aluminum corrosion.
Fig. 2 XRD patterns of residues after the hydration reactions of the sample (a) Al80 Ca20, (b) Al70 Ca30, and (c) Al50 Ca50, respectively.
was attached with the FE-SEM apparatus to distinguish the product mixture. High-resolution photo of the residual particles was observed using a transmission electron microscope (TEM, JEOL, JEM-2100F, 200 kV). The powder was dispersed in the ethanol, skimmed from the solution using copper grid. The change of pH during the hydration reaction was monitored using pH meter.

1.2.3. Results and discussions

Fig. 2 shows XRD patterns obtained from the products after the hydration reaction of reactant mixtures; (a) Al80 Ca20, (b) Al70 Ca30, and (c) Al50 Ca50. In Fig. 2(a), the product was mainly composed of bayerite [Al(OH)₃]. The broad peaks originated from bayerite, especially at 20 = 37–40 °, were due to the mixture of amorphous and crystalline phases. Some peaks originating from katoite, Ca₃Al₂[(OH)₄]₃, were also detected in the spectrum. The katoite has a cubic structure with \textit{Ia}₃\textit{d} space group, the same as grossular Ca₃Al₂[SiO₄]₃. The hydrogrossular series, Ca₃Al₂[SiO₄]₃ and Ca₃Al₂[(OH)₄]₃, can accommodate large quantities of water.\cite{6,7} The products including katoite might contain the water inside the lattice during the hydration reaction. The peak intensity of katoite became stronger in Fig. 2(b) than that shown in Fig. 2(a), and the main product in Fig. 2(c) was katoite which had high crystallinity. Volume ratio of katoite in the products gradually increases as the ratio of Ca(OH)₂ in the reactant increases from Fig. 2(a) to(c). The author have confirmed that almost all the reactants were converted into katoite after the hydration reaction when the weight ratio of Ca(OH)₂ increased up to 70 wt.%. The products after the hydration reaction were insoluble and cement-like adhesive powder with a gray color, and tended to adhere at the bottom of glass pot. SEM photos of the residues after the hydration reaction of Al80 Ca20, Al70 Ca30, and Al50 Ca50 samples are shown in Fig. 3(a)–(c), respectively. The crystal which had hexagonal shape crystal with a diameter of 2–3 μm might indicate the katoite because the katoite is classified as cubic class with high symmetry. The katoite crystals were surrounded with another small sediment that had whisker
Fig. 3 FE-SEM photos of the hydrated samples of (a) Al80 Ca20, (b) Al70 Ca30, and (c) Al50 Ca50, respectively. EDX signals at the point of (i) and (ii) in (a) and (c) are shown in (d-i) and (d-ii), respectively.
shape with a dimension under ~800 nm. XRD spectra in Fig. 2 indicated that the whisker might be identified as Al(OH)$_3$ phase. EDX spectra obtained from the point focused on the katoite crystals in Fig. 3(a) and (c) are shown in Fig. 3(d-i) and (d-ii), respectively. Four peaks attributed to OK$_\alpha$, Al K$\alpha$, CaK$\alpha$ and CaK$\beta$ were detected at 0.5, 1.5, 3.6 and 4.0 keV, respectively. However, both the CaK$\alpha$ and CaK$\beta$ peaks were not detected at the whisker. The peak of CaK$\alpha$ and CaK$\beta$ in Fig. 3(d-ii) is larger than that in Fig. 3(d-i) depending on the weight ratio of Ca(OH)$_2$; therefore, the hexagonal crystal could be identified to be katoite. In addition, the shape of the katoite crystal changed from hexagonal into polyhedron. The shape or size of whisker originated from Al(OH)$_3$ was almost the same among each sample.

Fig. 4 shows a distribution of aluminum, calcium, and oxygen ions of hydrated residues composing katoite and Al(OH)$_3$ at the area of 15 $\mu$m $\times$ 15 $\mu$m. Each area surrounded by red or green broken lines in CP image is crystalline hexagonal phase and whisker, respectively. The red area showed the distribution of Al, Ca, and O ions; however, the green one showed the existence of Al and O ion only. It was estimated that the hexagonal (red) and whisker (green) area showed katoite and Al(OH)$_3$, respectively, because the Ca ion exists only at the katoite particle. Fig. 5 shows TEM photos of (a) katoite and (b) Al(OH)$_3$ containing the dried residue of Al80 Ca20 after the hydration reaction. The corresponding selected-area electron diffraction (SAED) patterns are also inserted at the left corner of each photo. The katoite had a hexagonal with a diameter of 10 $\mu$m and showed polycrystalline. The katoite was surrounded with Al(OH)$_3$ powder precipitated in the solution. The SAED pattern taken from the surrounding Al(OH)$_3$ whisker in Fig. 5(b) showed broad and blurred diffraction rings, presumably due to a mixture of amorphous and polycrystalline phases. These results were consistent with existence of amorphous and crystalline phases in the XRD patterns in Fig. 2(a). Fig. 6(a) indicates the change of pH (circle) and the temperature of solution (triangle) during the hydration reaction. The magnification until 20 min was also shown at the upper corner.
Fig. 4 Elementary distribution of oxygen, calcium, and aluminum in the hydrated samples of Al50 Ca50. CP indicates comp image. The areas surrounded by red or green broken lines show katoite or Al(OH)₃ particles, respectively.
Fig. 5 TEM image of (a) katoite and (b) Al(OH)$_3$ area containing the dried residue of Al80 Ca20 that were obtained after the hydration reaction, respectively. The corresponding selected-area electron diffraction (SAED) patterns taken from each body are also inserted in the left corner.
Fig. 6 (a) The plots of pH and temperature of the solution containing Al50 Ca50sample. Magnification between the start and 20 min is shown at the corner of the same figure. (b) Calculated aluminum solubility diagram in equilibrium with amorphous Al(OH)$_3$ in 25°C. The inset at the corner indicates an enlarged diagram between pH = 10 and 14.
The Ca(OH)$_2$ has poor solubility in the water (0.17 g/100 mL at 25°C) in comparison with NaOH and its saturated solution shows at most pH 12.4–12.5 at room temperature. The hydrogen gas generated vigorously until 10 min and it gradually decreased below the lower limit of the flow meter. The pH plots could be divided into three terms: I (0–4 min), II (4–10 min), and III (10 min – end).

At first, the pH showed 12.5 and it suddenly dropped into 10.9 within 4 min due to the consumption of OH ions. On the term II, the pH kept the same value and slightly decreased into 10.7. On the term III, it gradually increased as the solution temperature decreased and reached 11.5. The amorphous Al(OH)$_3$ shown in Fig. 5(b) is known for its amphoteric characteristic, resolving in either strong acid or alkali solution as follows:

$$\text{Al(OH)}_3 + 3\text{H}^+ \rightleftharpoons \text{Al}^{3+} + 3\text{H}_2\text{O} \quad (6)$$

$$\text{Al(OH)}_3 + \text{OH}^- \rightleftharpoons \text{Al(OH)}_4^- \quad (7)$$

Fig. 6(b) shows the calculated the aluminum solubility diagram in equilibrium with amorphous Al(OH)$_3$ at 25°C based on the equilibrium (6) and (7). The inset at the corner indicates the enlarged ion concentration between pH = 10 and 14 in the same diagram. The aluminum solubility during the terms I and II in Fig. 6(a) corresponds to the magnification in the inset in Fig. 6(b). It was clear that the aluminum solubility depended on the pH change strongly. The water molecules in the hydration shell are progressively replaced by hydroxyl ions, giving negative charge, according to the following sequence:

$$\text{Al}^{3+} \rightarrow \text{Al(OH)}^{2+} \rightarrow \text{Al(OH)}_2^+ \rightarrow \text{Al(OH)}_3 \rightarrow \text{Al(OH)}_4^- \quad (8)$$

The hydrolysis scheme above would proceed from left to right as the pH increased. The soluble anion Al(OH)$_4^-$ becomes dominant in our experiment considering the change of pH from 12.5 to 10.7 in Fig. 6(a). The insoluble Al(OH)$_3$ would precipitate as the pH of the solution decreased. The temperature of the mixture increased up to ~94 °C within 10 min with a plateau at 3 min with an evolution of hydrogen gas, and it gradually decreased after the generation of hydrogen gas ended.
Fig. 7 (a) A plotted curve obtained from a gas chromatography during the hydration reaction. (b) Volume change of hydrogen gas about Al80 Ca20, Al70 Ca30, and Al50 Ca50 obtained from gas flow meter. Each change of the solution temperature containing the samples is also shown in (c).
Then, the author could estimate that more than two chemical reactions progressed with a generation of hydrogen gas. Fig. 7(a) indicates a general appearance of plotted curves obtained from a gas chromatography during the hydration reaction. The strong peak at 4.90 min, small dips at 10.3 and 11.1 min in the retention time show hydrogen, nitrogen and oxygen gas, respectively. That is, almost all the produced gas during the reaction was identified as hydrogen. The N₂ and O₂ peaks are due to the mixture of residual air from the glass pot. Fig. 7(b) shows a volume change of hydrogen gas about Al₈₀Ca₂₀, Al₇₀Ca₃₀, and Al₅₀Ca₅₀ as a function of reaction time. The change of the velocity of hydrogen gas generation (mL/min) is also plotted at the right corner of the figure. In case of 80Al 20Ca, I stopped the reaction at 40 min due to the dangerous runaway reaction derived from the corrosion of excess aluminum powder. The profile of the volume change can be divided into two terms: 0~20 min (shade area) and 20~80 min. (The hydrogen gas generation was completed at 70 min.) The maximum of the velocity of hydrogen gas generation within 8~11 min decreased from 460 to 360 mL/min as shown in the inserted figure when the weight ratio of aluminum in the reactant powder decreased from 70Al 30Ca to 50Al 50Ca. However, both reaction rates in 70Al 30Ca and 50Al 50Ca showed more than 99% calculated from the total volume of the hydrogen gas. The reaction rate of 80Al 20Ca was calculated to be 95% at most. Fig. 7(c) shows the temperature dependence of the solutions as a function of reaction time. The magnification till ~30 min is also shown at the corner. In case of 80Al 20Ca, the temperature increased from 23 °C to 45 °C within 10 min, shown within the shaded area, and runaway reaction started. In case of other samples, the temperature increased for more than 15 min and showed a plateau term. Moreover, it increased again and reached at 60 °C(50Al 50Ca) or 70 °C (70Al 30Ca) after 50~60 min. Each XRD profile of the sample Al₅₀Ca₅₀ at 7, 35, and 65 min later in Fig. 8(I) was shown in Fig. 8 II(a), (b), and (c), respectively. These samples were prepared by filtering the sample using a filter paper to remove the water at each time. Both Al(OH)₃ and katoite were produced within the term (a), however, the main
Fig. 8 (I) Typical volume change of hydrogen gas as a function of time. XRD patterns of the residues left after the hydration reaction at (a) 7, (b) 35, and (c) 65 min later within I(a)–(c) are shown in II(a)–(c), respectively.
component was identified as unreacted aluminum. At the term (b), the ratio of katoite increased and the unreacted aluminum decreased. At the term (c), almost all products were identified as katoite and Al(OH)$_3$ and unreacted aluminum was not observed. In addition, the amount of Al(OH)$_3$ was increased from Fig. 8II(b) to (c). Fig. 9 shows a model of the chemical reactions in the mixture. I suppose that the corrosion reactions would proceed from the stage 1 to 4. Considering the existence of surface oxide on the surface of aluminum particle, the author propose the following equilibrium reactions at the stage 1 and 2:

$$\text{Al}_2\text{O}_3 + \text{H}_2\text{O} \rightleftharpoons 2\text{AlOOH} \quad (9)$$

$$\text{AlOOH} + \text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_3 \quad (10)$$

$$\text{Al(OH)}_3 + \text{OH} \rightleftharpoons \text{Al(OH)}_4^- \quad (11)$$

$$3\text{Ca}^{2+} + 2\text{Al(OH)}_4^- + 8\text{H}_2\text{O} \rightleftharpoons \text{Ca}_3\text{Al}_2(\text{OH})_{12} + 6\text{H}_2 \quad (12)$$

Suppose that the Al$_2$O$_3$ shown in (9) is different from bulk α-Al$_2$O$_3$ with a corundum structure. [9] The thin passive layer reacted with water and disruption of Al–O–Al bonds occurs via hydrolysis reaction to form Al–OH species. The alkali solution accelerated the reaction effectively. It was reported that one Al–O–Al linkage is broken to form two Al–OH for each water molecule consumed in the hydrolysis reaction [9]. The water molecule tends to attack the aluminum through the pits that contain the passive layer and hydration reaction proceeded. Then, extensive hydration propagates the formation of boehmite, γ-AlOOH, or aluminum hydroxide, Al(OH)$_3$, that are thermodynamically more stable than Al$_2$O$_3$ at room temperature in hot water following (9) and (10). [10] The amorphous Al(OH)$_3$ tends to dissolve into Al(OH)$_4^-$ ion in strong alkali solutions as shown in (11), resulting in the formation of seeds and the growth of katoite via the reaction among Ca$^{2+}$, Al(OH)$_4^-$ ions and water molecule following the reaction (12). One of the characteristics of the chemical reaction is in the easy controllability of the speed of hydrogen release by controlling the reactions shown in (9)–(12). In Fig. 7(b), the term between the start and the first shoulder in the curve, as
shown in the shaded area, increased in proportion to the increase of weight ratio of Ca(OH)$_2$ in the starting materials due to the progress of katoite formation shown in the stage 1 and 2 in Fig. 9. At the stage 3, hydration of aluminum powder mainly progressed with the release of hydrogen gas following the reactions (1)–(3) after the surface oxide dissolved into the solution and localized breakdown occurred shown in the figure (red circle). The aluminum hydration further progressed and the bare aluminum was converted into insoluble Al(OH)$_3$, which had a whisker shape, and polycrystalline katoite crystals in Fig. 3(a)–(c). As these reactions proceeded, the size of aluminum decreased as shown in the stage 4 and it finally dissolved into the solutions completely and the release of hydrogen stopped. The weight ratio of the Ca(OH)$_2$ is one of the important factors to release the hydrogen gas from the corrosion reaction of aluminum powder. The initial pH in the solution was almost the same in all the samples; however, the reaction rate of the aluminum corrosion depended on Ca(OH)$_2$ content. The release of hydrogen gas was originated from both the katoite formation and hydration of aluminum. The OH ion helps the destruction of passive layer at the surface of aluminum powder and makes a pit to pass the water molecule. However, the aluminum hydration produces gel-like amorphous Al(OH)$_3$ to obstruct the pit, resulting in the termination of the reaction. In addition, the lack of Ca(OH)$_2$ tended to promote the runaway reaction as shown in 80Al 20Ca sample. That is, the appropriate addition of Ca(OH)$_2$ promotes the crystal growth of katoite shown in stage 2 in Fig. 9, and realized the good controllability of aluminum corrosion with the moderate release of hydrogen gas.4.
Fig. 9 Model of the aluminum corrosion in Ca(OH)$_2$ solution. The corrosion reactions progress from the stage 1 to 4.
1.2.4 Conclusions

The author demonstrated the controllable hydrogen release via the corrosion of aluminum powder in Ca(OH)$_2$ solutions. The corrosion mechanism of the aluminum in the solution was analyzed using various surface analyses of residues and the plot of pH change in the solution in detail. It was estimated that the mechanism included katoite formation and hydration of aluminum; the katoite formation has an important factor to proceed with the aluminum corrosion and generate the hydrogen gas moderately.

1.2.5 References


1.3 Design of Controllable Hydrogen Generation System using Al Foil

1.3.1 Introduction

Hydrogen production is one of the most crucial technologies in the usage hydrogen itself for fuel cells. Because fuel cells directly convert the chemical energy in hydrogen to electricity, with pure water and potentially useful heat as the only byproducts. [1] In general, hydrogen is commercially produced by steam reforming, partial oxidation, or thermal cracking of hydrocarbons, biomass gasification, and electrolysis under alkaline media.[2-6] Produced hydrogen is stored into the compressed tank under ~70MPa. [7] In this system, the weight and volume of the storage cylinder are major disadvantages. In order to meet the requirements for small power generators, decomposable chemical hydrides, which release hydrogen by hydrolysis reactions, appear to be attractive alternatives to compressed hydrogen gas. [8-13] However, chemical hydrides are ‘water-sensitive’: in contact with water they can generate flammable and undergo a vigorous reaction. Such reactions can cause overpressure in sealed equipment or pipework. With flammable gas generation the heat of reaction may cause ignition, depending upon the compound in question. [14, 15]

Aluminum corrosion reaction is an alternative method to produce hydrogen for a fuel cell. One gram of aluminum can produce 1.33 L of hydrogen from water at 20 °C under 1 atm. Though this method is not energetically efficient because the energy required for producing aluminum is greater
than that for producing hydrogen from water, this on-demand hydrogen-production method has potential advantages of good availability, mobility, and stability of reactants. To generate hydrogen, aluminum powder has been commonly used in the aluminum-water system [16-18]. However aluminum powder is very reactive and may cause dust explosions. [19, 20]

Here, the author employed the aluminum foil to avoid the risk and successfully demonstrated the time control of hydrogen gas release in calcium hydroxide Ca(OH)$_2$ solutions.

1.3.2 Experimental

Chemicals

Aluminum foil was supplied from UACJ Corporation. Ca(OH)$_2$ was purchased from NACALAI TESQUE, INC. as extra pure reagent (>95.0%).

Reaction

Steeping Reaction [Fig.1 (a)]

A mixture of Al foil (1g) and Ca(OH)$_2$ (1g) was put into a 100 ml flask. And then 25 ml of distilled water was poured into the flask.

Effect of various thickness of Al foil with same area by Stirring Reaction [Fig.4]

A mixture of 80 sheets of Al foil (each size: 25mm × 25mm square) and 1g of Ca(OH)$_2$ was put into a 500 ml separable flask. The total weight of aluminum foil in each thickness from 6.5μm to
100μm is 1.01, 1.66, 2.19, 2.56, 6.55 and 13.24g, respectively. After 300 ml of distilled water was poured into the flask, the reaction mixture was stirred.

Effect of various area of Al foil with same thickness by Stirring Reaction [Fig. 6]

A mixture of predetermined amount of Al foil (thickness: 12μm, each size of Al foil piece: 25mm x 25mm square) and 1g of Ca(OH)$_2$ was put into a 500 ml separable flask. The total area of aluminum foil in each experiment is $100 \times 250 \text{ mm}^2$ (x1), $200 \times 250 \text{ mm}^2$ (x2), $300 \times 250 \text{ mm}^2$ (x3) and $400 \times 250 \text{ mm}^2$ (x4), respectively. After 300 ml of distilled water was poured into the flask, the reaction mixture was stirred.

In each reaction, the flow rate and total amount of generated gas was monitored using a high precision film flow meter on a HORIBA STEC VP-2U. The component of the produced gas was analyzed using gas chromatography. Gas chromatography (GC-TCD) was carried out on a Shimadzu GC-2014 equipped with a SHINCARBON ST column (6 m). The change of pH during the corrosion reaction was monitored using pH meter.

Analysis Techniques.

The crystal phases of the synthetized product were determined by X-ray Diffraction (XRD). XRD measurements were carried out on a Rigaku Multi-Purpose X-ray Diffractometer (Ultima IV) by using Cu Kα-radiation at 40 kV and 40 mA.

The particle size and morphology of the synthetized powders were observed by using a Scanning
Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS) JSM-6700F JED-2300, Japan Electronics Co. with an accelerating voltage of 5 kV for SEM and 15 kV for EDS analysis.

Bond vibrations analyses of the active materials were analyzed by Raman spectroscopy (NRS3100, JASCO CORPORATION) with green laser (532 nm) as source.

Time of flight secondary ion mass spectrometry (TOF-SIMS) analysis was performed using a TRIFT IV nano TOF (ULVAC-PHI, Japan) spectrometer. Negative secondary ion spectra were obtained using a 30 Kev Au\(^{3+}\) gold trimer ion at a current of 3 nA, with a pulse width of 18.0 ns. Mass number ranges of 0–1800 were applied.

1.3.3 Results and Discussion

Fig. 1(a) shows the result of hydrogen generation experiment which was carried out in the Ca(OH)\(_2\) aqueous solution with Al kitchen foil. It was confirmed that the generation rate of hydrogen gas in this system continued gradually over 2 hours and the yield of hydrogen obtained above 90%.

This result signifies that aluminum foil has the probability as the stable hydrogen generator in contrast to the aluminum powder. Fig. 1(b) indicates a general appearance of plotted curves obtained from a gas chromatography during the corrosion reaction. The strong peak at 3.6 min, small dips at 9.6 and 11.1 min in the retention time show hydrogen, oxygen and nitrogen gas, respectively. That is, almost all the produced gas during the reaction was identified as hydrogen. The N\(_2\) and O\(_2\) peaks are
Fig. 1 Diagram of (a) Hydrogen production rate and total amount curve obtained for 12μm Al foil in Ca(OH)$_2$ aq. at 20°C, and (b) A plotted curve obtained from a gas chromatography of produced gas.
chemical composition, reaction rate and generation time of hydrogen gas in different types of Al foil due to the mixture of residual air from the glass flask. Encouraged by this result, the author next investigated the detail potential of aluminum foil for hydrogen generation reaction. The thickness, defined by Japanese Industrial Standards (JIS) are summarized in Table 1. The Al foil defined as 1N30 and 1085 has more impressive ability than 8021 and 8079 in the reaction rate and the generation time of hydrogen gas.

The detail differences between 1N30, 8021 and 8079 were examined by ToF-SIMS. Fig.2 shows the fragmentation ions detected by the mass spectrograph. These ions were derived from the oxide layer on the surface of Al foils. The normalized intensity of 8079 exhibited the highest peak in every fragmentation ions. Furthermore, the linear relationship between the normalized intensity of total fragmentation ion and the reactivity of aluminum foil was found. (Fig.3) It was supposed that the thickness of oxide layer on the surface of Al foil had one of the most effective factors in this reaction system, and the trend of oxide layer was depending on the purity of aluminum in Al foil.

As the results of above-mentioned, 1N30 and 1085 was superior material to generate hydrogen gas. Above all, 1N30 was thought to be best material to investigate the ability of aluminum foil, because 1N30 is produced on a large scale for customer use and the cost is very economical compared to 1085. So, 1N30 was employed as a reference material.

At first, the effect of the Al foil thickness was examined. Fig.4 shows the hydrogen generation rate
Table 1  The results of corrosion reaction by various type of Al foils

<table>
<thead>
<tr>
<th>Al foil</th>
<th>Thickness (μm)</th>
<th>Composition (wt%)</th>
<th>Reaction rate of Al (%)</th>
<th>Generation time of H₂ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1N30</td>
<td>12</td>
<td>Si + Fe 0.70</td>
<td>99.2</td>
<td>91</td>
</tr>
<tr>
<td>1085</td>
<td>15</td>
<td>0.1</td>
<td>99.78</td>
<td>87</td>
</tr>
<tr>
<td>8021</td>
<td>12</td>
<td>0.15</td>
<td>98.15</td>
<td>73</td>
</tr>
<tr>
<td>8079</td>
<td>12</td>
<td>0.3</td>
<td>98.4</td>
<td>64</td>
</tr>
</tbody>
</table>

*a reaction conditions: Al 1g, Ca(OH)₂ 1g, H₂O 90ml, temperature 20 ºC. **The number of Al foil is based on Japanese industrial standard (JIS).

![Graphs showing normalized intensity of fragmentation ions measured by Time of Flight Secondary Ion Mass Spectrometry](image)

**Fig.2** Normalized intensity of fragmentation ions measured by Time of Flight Secondary Ion Mass Spectrometry
Fig. 3 The relationship between normalized intensity of total fragmentation ions and reaction rate of aluminum.
Fig. 4 Hydrogen production rate obtained for various thickness of Al foils, the magnification until 3 h at the upper corner.

Fig. 5 The relationship between hydrogen generation time and the thickness of Al foil.
(ml/min) and time (h) of aluminum corrosion reaction. In the beginning of reaction, hydrogen generation rate in every types of Al foil was dropped. This common reactivity may be due to the removal of aluminum oxide formed on the surface of Al foil as passive layer, and then, the generation rate recovered. The generation time of hydrogen got longer with the increasing of the thickness of Al foil. Notably, in the case of 100 μm of Al foil, the generation time of hydrogen recorded more than 24 hours. Furthermore, the correlation between the thickness from 6.5 to 100 μm of Al foil and the generation time indicated the first order as shown in Fig.5. This results support the hydrogen generation time is controllable by the selection of Al thickness.

The effect of various area of Al foil under same thickness (12μm) was also verified. The area was controlled from x1 to x4 described in experimental section. The gain in area of aluminum foil leads to increase of generation rate of hydrogen gas. (Fig.6) It can clearly be seen that the relation of average in generation rate versus area of aluminum foil was also first order, as noted in Fig.7.

Fig.8 shows time course of pH value and generation rate (ml/min) of hydrogen gas in the reaction. Interestingly, the profile of the pH data was almost same to that of hydrogen generation rate. Since the gap between these two profiles is due to the time deviation of film flow meter, this change seems to proceed simultaneously.

The weight control of Ca(OH)$_2$ under the condition of aluminum corrosion reaction was examined. As shown in Fig.9, the results proved that the appearance of minimum point in the
Fig. 6 Hydrogen production rate obtained from various areas of 12 μm Al foils

Fig. 7 The relationship between average of generation rate and the area of 12μm Al foil.
generation rate was depending on the amount of Ca(OH)$_2$. Finally, when the ratio of aluminum to Ca(OH)$_2$ was 1:1.1, the minimum point was disappeared. The fluctuation of the generation rate comes concurrently with the change of pH value as described in Fig.8. The results obtained from the weight control of Ca(OH)$_2$ is also thought to be brought about by the effect of OH$^-$ concentration. With the addition of Ca(OH)$_2$, it is believed that the diffusion of the OH$^-$ ion from solid phase to liquid phase is faster, and then the pH of solution will be keeping high value.

The generation rate of hydrogen gas by aluminum corrosion reaction is up-and-down under the low concentration of Ca(OH)$_2$, so the residue and surface of Al foil in each stage was investigated in each stage. (Fig.10)

Fig.11 shows the X-Ray Diffraction (XRD) patterns of the residue from stage 1 to stage 4. As the reaction proceeded, the consumption of Aluminum, Ca(OH)$_2$ and CaCO$_3$, which is produced by the reaction of saturated aqueous Ca(OH)$_2$ with CO$_2$ dissolved in the solution, is confirmed. The residue shows diffraction peak due to the Ca$_3$Al$_2$O$_6$(H$_2$O)$_6$ and Ca$_4$Al$_2$(OH)$_12$(CO$_3$)(H$_2$O)$_5$ in addition to diffraction peak of the simple hydration product such as Al$_2$O$_3$ and $\alpha$-Al(OH)$_3$.

Fig.12 shows Raman spectrum of the surface of aluminum foil in each stage. The band observed around 930 and 1061 cm$^{-1}$ are corresponding to the $\delta$(OH) vibrations of the hydroxyl groups (in the bayerite structure). Al-O stretching presents the following bands as reported in the literature: 306 and 371 cm$^{-1}$ (due to gibbsite). [21] The signal around 530 cm$^{-1}$ might be due to the
Fig. 8 Time course of hydrogen generation rate and pH value.

Fig. 9 The weight effect of Ca(OH)$_2$ in the corrosion reaction of 12 μm Al foil (Al: 1.66 g, H$_2$O: 300 ml)
Fig. 10 Investigation point of aluminum foil and its residue [Al:1.66g, Ca(OH)$_2$:1g, H$_2$O:300ml]

Fig. 11 X-Ray Diffraction patterns of residue for aluminum corrosion reaction in each stage
Fig. 12 Raman Spectra of surface of aluminum foil for aluminum corrosion reaction in each stage.
structure of [AlO$_4$]$^3^-$, which is the component of the calcium aluminate structure confirmed by the XRD measurement. Fig. 13(a) shows the SEM images of surface on the aluminum foil for different time from stage 1 to stage 4. It can be observed that considerable change in the microstructure of the materials occurred with the increase of reaction time. As can be seen in stage 1 in Fig. 1(a), the deposit with dendritic structure was confirmed, and the material was getting bigger until stage 3. At stage 4 in the end of the reaction, the deposit was seemed to be removed from the surface and polygon shaped particles (2-3 μm in diameter) was observed on the surface of aluminum foil.

Fig. 13 (b) shows the EDS mapping of the surface on the aluminum foil in Fig. 13 (a) for Al, O, and Ca elements respectively. Coexisting states of Al, Ca and O were confirmed in stage 2, 3 and 4 in Fig. 13 (b). Areas surrounded by black broken line of stage 2 in Fig. 13 (b) are pointing out as example. The particle sizes of these deposits are decreasing in stage 4. At present, these composite materials have been considered as Ca$_3$Al$_2$O$_6$(H$_2$O)$_6$ or Ca$_4$Al$_2$(OH)$_{12}$(CO$_3$)(H$_2$O)$_5$.

As illustrated in Scheme 1, (I) the aluminum corrosion reaction possibly proceeds via attach of Ca$^{2+}$, OH$^-$ and CO$_3$$^{2-}$ ion to the oxide layer on the surface of aluminum. (II) Subsequently, the produced α-Al(OH)$_3$ and calcium aluminate such as Ca$_3$Al$_2$O$_6$(H$_2$O)$_6$ or Ca$_4$Al$_2$(OH)$_{12}$(CO$_3$)(H$_2$O)$_5$ are dispersed to the reaction solution. (III) Next step, H$_2$O react with the exposed aluminum and then hydrogen gas is generated. (IV) After stage 3 in Fig. 10, the hydrogen gas was generated in definite proportion under the stable pH condition.
Fig. 13 The surface of aluminum foil in each stage (a) SEM images of samples, (b) Elementary distribution of aluminum, oxygen and calcium.
Scheme 1  Possible reaction mechanism for the aluminum corrosion reaction

\[
\begin{align*}
\text{Al} & \quad \text{oxide layer (Al}_2\text{O}_3) \\
\text{H}_2\text{O} & \quad \text{H}_2\text{O} \\
\text{OH}^- & \quad \text{Ca}^{2+} \\
\text{H}_2\text{O} & \quad \text{H}_2\text{O} \\
\text{OH}^- & \quad \text{CO}_3^{2-} \\
\text{Ca}^{2+} & \quad \text{OH}^- \\
\text{H}_2\text{O} & \quad \text{CO}_3^{2-} \\
\text{Ca}^{2+} & \quad \text{OH}^- \\
\text{H}_2\text{O} & \quad \text{CO}_3^{2-} \\
\text{Ca}^{2+} & \quad \text{OH}^- \\
\text{H}_2\text{O} & \quad \text{CO}_3^{2-} \\
\text{Ca}^{2+} & \quad \text{OH}^- \\
\end{align*}
\]

\(\bigcirc\) : Calcium aluminate : \(\text{Ca}_3\text{Al}_2\text{O}_6(\text{H}_2\text{O})_6\) or \(\text{Ca}_4\text{Al}_2(\text{OH})_{12}(\text{CO}_3)(\text{H}_2\text{O})_5\)

\(\bullet\) : α-Al(\text{OH})_3
1.3.4 Conclusion

1N30 was the best aluminum foil to generate the hydrogen gas. Hydrogen gas was generated stably more than 24 hours by using 100μm aluminum foil in thickness. Generation time and rate of hydrogen gas was corresponding to the thickness and total area of aluminum foil.

1.3.5 References


Chapter 2

Application to Li ion Battery

2.1 Synthesis of Spinel LiNi$_{0.5}$Mn$_{1.5}$O$_4$ by a Wet Chemical Method and Characterization for Lithium-Ion Secondary Batteries

2.1.1 Introduction

LiCoO$_2$ has been commercialized as an attractive cathode material for a wide range of applications in electronic devices. [1-3] The high cost and toxicity of LiCoO$_2$ have promoted the search of new alternatives in cathode materials. [1] Transition metal oxides like LiMn$_2$O$_4$ are one of the material most studied due to their several advantages as low cost, abundance, and nontoxicity. [2-4] Spinel structure LiMn$_2$O$_4$ has a three dimensional Li$^+$ diffusion pass way. [5,6] It is expected to have better electrochemical properties than two-dimensional layered material. However, LiMn$_2$O$_4$ shows a poor cycling performance. Therefore, many investigations have been focused on transition metal-substituted spinel compounds, such as LiM$_x$Mn$_{2-x}$O$_4$ (M=Cr, Co, Fe, Ni, Cu). [7-15] The role of the doped metal ions on the Li/LiM$_x$Mn$_{2-x}$O$_4$ cell is to compensate for the capacity loss which originates from the oxidation state of Mn$^{3+}$ to Mn$^{4+}$ below 4.5 V by oxidizing M$^{2+}$ to M$^{4+}$ over 4.5V. [16, 17]

Among those doped materials, the Ni substituted LiMn$_2$O$_4$ spinel with the composition LiNi$_{0.5}$Mn$_{1.5}$O$_4$ is special interest because high capacity of 130-140 mAh/g with a high operating
voltage in the 5V range [1, 7, 17-28] and good electrochemical performance. In the charge-discharge process of the Li$_x$Ni$_{0.5}$Mn$_{1.5}$O$_4$ electrode, lithium ions are reversibly inserted into and extracted from the Li$_x$Ni$_{0.5}$Mn$_{1.5}$O$_4$ spinel phase in two composition ranges of 0$\leq$x$\leq$1 and 1$\leq$x$\leq$2 over two potential plateaus located at around 4.7V and 2.7V, respectively. [22] LiNi$_{0.5}$Mn$_{0.5}$O$_2$ has a rhombohedral layered structure with space group R3m, with lithium and transition metal ions in a close-packed oxygen array, leading to the formation of lithium and transition metal layers. [25] About 8–10 at.% of nickel and lithium ions can interchange their sites in the layered structure, which is often referred to cation mixing. [25]

The electrochemical performance is strongly dependent on the synthesis procedure. Various synthesis methods such as sol–gel method, [17, 29,30] solid-state method, [31-34] molten salt method, [35] co-precipitation, [1,21,36-37] ultrasonic spray pyrolysis method, [23] hydrothermal synthesis, [38] etc., have been used to synthetize LiNi$_{0.5}$Mn$_{1.5}$O$_4$. In general, the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ materials prepared by the conventional solid-state method presents large particle grain size and heterogeneous particles, while through the wet chemical methods like sol-gel and co-precipitation can provide LiNi$_{0.5}$Mn$_{1.5}$O$_4$ with narrow particle size distribution with highly homogenous composition and high discharge capacity. However, it is difficult to obtain higher active material LiNi$_{0.5}$Mn$_{1.5}$O$_4$ due to the substantial Li/Ni disorder [39] or structural impurity. [17, 40, 41]

It is important to synthetize pure phase LiNi$_{0.5}$Mn$_{1.5}$O$_4$ due to the presence of non-stoichiometric
spinel which deteriorates its electrochemical performance. In this chapter, the structural and electrochemical properties of LiNi_{0.5}Mn_{1.5}O_{4} spinel by a simple wet chemical method was studied. A pure phase of LiNi_{0.5}Mn_{1.5}O_{4} spinel was obtained and the structure and electrochemical properties were compared with a commercial standard sample.

2.1.2 Experimental

Synthesis

Two samples of LiNi_{0.5}Mn_{1.5}O_{4} spinel were synthesized from acetates precursors by wet chemical method. They were prepared at different chemical composition. The first one (LNMO-1) raw materials molar ratio is (Li/Mn=0.66, Li/Ni=2.38, Ni/Mn=3.59) and another one (LNMO-2) raw materials molar ratio is (Li/Mn=0.67, Li/Ni=2.01, Ni/Mn=3.00). The following compounds were used: Mn(CH_{3}COO)_{2}·4H_{2}O (Nacalai 99.0%), Ni(CH_{3}COO)_{2}·4H_{2}O (Nacalai, 98.0%), LiOH·H_{2}O (Nacalai, 99.0%). The LiNi_{0.5}Mn_{1.5}O_{4} commercial reagent (Aldrich, <0.5 μm particle size by BET, >99% purity) was employed to compare the electrochemical behavior, dried in an evaporator between 40 to 10 hPa. First, the stoichiometric Ni(CH_{3}COO)_{2}·4H_{2}O (0.78 g) and Mn(CH_{3}COO)_{2}·4H_{2}O (2.73 g) were dissolved in 17 ml and 49.4 ml of distilled water, respectively. Then, both solutions were mixed into a flask under constant stirring. LiOH·(H_{2}O) (0.31 g) was added to the above solution. The mixture was refluxed at 100-110°C for 5 hours and then it was dried in an
evaporator between 40 to 10 hPa. The drying process was completed at 130 °C. After, the obtained powder was pulverized by using an agate mortar. Pre-calcination of the sample was performed at 600 °C for 2 hours in air. After the obtained powder was pulverized by using an agate mortar, calcination was performed at 800°C for 1 hour. The same procedure was performed for the synthesis of LNMO-2 with the variation in the stoichiometric amount of raw materials: 2.66 g of Ni(CH$_3$COO)$_2$·4H$_2$O, 7.78g of Mn(CH$_3$COO)$_2$·4H$_2$O and 0.893 g of LiOH·(H$_2$O). The sample LMNO-1 has higher amount of Mn/Ni precursor.

Analysis Techniques.

The crystal phases of the synthetized product were determined by X-ray Diffraction (XRD). XRD measurements was carried out on a Rigaku Multi-Purpose X-ray Diffractometer (Ultima IV) by using Cu Kα-radiation at 40 kV and 40 mA.

The particle size and morphology of the synthetized powders were observed by using a Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS) JSM-6700F JED-2300, Japan Electronics Co. with an accelerating voltage of 5 kV for SEM and 15 kV for EDS analysis.

Bond vibrations analyses of the active materials were analyzed by Raman spectroscopy (X-Plora, Horiba, Ltd.) with green laser (532 nm) as source.

Analysis of the chemical state of the elements were analyzed by X-Ray Photoelectron Spectroscopy (XPS) ESCA 5800, Ulvac-Phi Inc., by using Al Kα 10 kV as X-rays source at 58.7 eV and vacuum
at 2\times 10^9 \text{ Pa}.

**Electrochemical tests**

The cathode pellets were prepared by mixing cathode materials with acetylene black as conducting agent and polyvinylidene fluoride (PVDF) as binder, in a ratio of 85:10:5. The materials were pressed in an aluminum mesh and drying in an oven at 80°C for 8 h.

The charge and discharge measurements were conducted using stainless two electrode cell. The cells were assembly in an Ar-filled glove box using 1.0 M/L of LiPF$_6$ in ethylene carbonate (EC) and diethyl carbonate (DEC) with volume ratio of 1:1 as electrolyte and metallic lithium foil as counter electrode. The configuration of the cell is as follows: Li | 1M LiPF$_6$ in EC/DEC(v/v=1/1) | LiNi$_{0.5}$Mn$_{1.5}$O$_4$.

The charge and discharge tests were performed between 3.5 and 4.9 V at 0.3C.

### 2.1.3 Results and Discussion

![Image](image.png)

Figure 1, shows the X-Ray Diffraction (XRD) patterns of the synthetized cathode materials LNMO-1, LNMO-2 and the commercial one. The results show the same diffraction peaks than the commercial one, corresponding to the crystal phase of spinel LiNi$_{0.5}$Mn$_{1.5}$O$_4$ in the structure Fd3m. [22, 42] XRD However, the sample LNMO-2 shows a slightly additional peaks correspond to the by-products of Li$_{(1-x)}$NiO and Ni$_3$MnO$_8$. 
Figure 2 shows the SEM images of the synthetized materials and the commercial one. It can be observed that LNMO-1 and LNMO-2 present small particles at the nanorange order and polyhedral morphologies with smooth surfaces. The sample LNMO-1 presents a particle size distribution between 100 nm to 300 nm and the sample LNMO-2 between 50 nm to 300 nm. It can be observed that LNMO-1 has higher homogeneity than the LNMO-2. The LNMO-commercial shows small particles around of 50 nm but a high agglomeration.

Figure 3 shows Raman spectrum of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ synthetized materials. The signals observed around 619 cm$^{-1}$ are corresponding to the Mn-O stretching vibration of the MnO$_6$ octahedral. Mn-O stretching presents the following bands as reported in the literature: 625 (symmetric Mn-O stretching vibration of MnO$_6$ groups), 580, 483, 426, and 362 cm$^{-1}$, assigned to $A_{1g}$, $F_{2g}^{(3)}$, $F_{2g}^{(2)}$, $E_g$, and $F_{2g}^{(1)}$ modes, respectively, as predicted by group theory for a cubic compound. [43,45] The signals around 476 cm$^{-1}$, and 378-382 cm$^{-1}$ are corresponding to the Ni$^{2+}$—O stretching vibration. [43] Moreover the presence of those signals confirm the presence of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ in the Fd3m spinel.

The symmetric Mn-O stretching vibration of MnO$_6$ octahedral shifts slightly to lower wavenumber for the synthetized samples specially LMNO-1, indicating that the Ni$^{2+}$ ions amount and charge affects the MnO$_6$ symmetry. Probably it is caused by the increase of the average valence state of Mn ions.
Fig. 1 X-Ray Diffraction patterns of active materials: (a) LNMO-commercial (b) LNMO-1 (c) LNMO-2
Fig. 2 Scanning Electron Microscopy images of active materials: (a) LNMO commercial (b) LNMO-1 (c) LNMO-2

Fig. 3 Raman Spectra of the active materials: (a) LNMO-commercial (b) LNMO-1 (c) LNMO-2
The band around 564 cm\(^{-1}\) is a shoulder band of the Mn-O (F\(_{2g}\) band) originates mainly from the vibration of the Mn\(^{4+}\)-O bond. The intensity of this band is enhanced upon nickel substitution. [43] The well split separation of these two bands (A\(_{1g}\) and F\(_{2g}\)) is attributed to the Ni\(^{2+}/\)Mn\(^{4+}\) cation ordering in the material. [44] As shown in figure 3 this peak is clearly remarked and well splitted for the commercial sample but not for the synthetized one. This might be due to the change of the Mn\(^{3+}/\)Mn\(^{4+}\) ratio vs Ni\(^{2+}\) in the material, which indicates that the commercial sample has a higher amount of Ni\(^{2+}\) than those synthetized one, also indicating an average Mn oxidation state close to +4 in the commercial one. In another way, it can be deduced that the cation ordering was partially depressed on the synthetized samples.

Figure 4 shows the X-Ray Photoelectron Spectroscopy (XPS) spectra of Ni 2p and Mn 2p of LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\) powders. The Ni 2p spectrum shows signals of Ni 2p\(_{3/2}\) with binding energies of 854.0 eV for all the samples, corresponding to the oxidation state of Ni\(^{2+}\). [44,46] The Mn 2p spectrum shows two signals due to Mn 2p\(_{3/2}\) at 641.7 eV and Mn 2p\(_{1/2}\) at 653.6 eV. The signals of Mn 2p\(_{3/2}\) are used to determine the surface oxidation state of Mn. The signal of Mn 2p\(_{3/2}\) with binding energy of 642.5 eV corresponds to Mn\(^{4+}\) and the other one with 641.6 eV corresponds to Mn\(^{3+}\). [44] The samples showed Mn 2p\(_{3/2}\) at 641.6 eV indicating that the main oxidation state of surface Mn ions is +3 but a little contribution of +4 is obtained by peak separation of Mn 2p\(_{3/2}\) peak. There is
Fig. 4 X-Ray Photoelectron Spectroscopy spectra of Ni2p (left) and Mn2p (right) for the synthetized samples and the commercial one. (a)LMNO-Commercial (b) LNMO-1 (c) LMNO-2
not a big difference in the oxidation states for the synthetized samples and the commercial one. The atomic concentration obtained by XPS results is observed in the table 1. It can be observed than at the surface level the two synthetized samples presents higher Mn/Ni ratio than the commercial one as in concordance with the Raman results.

Table 2 shows the composition obtained by The Inductively Coupled Plasma (ICP). The synthetized LNMO-1 presents the least amount of nickel than LNMO-2 and the commercial one.

Figure 5 shows the initial charge-discharge curves of the synthetized and commercial samples. The charge/discharge capacity values and the initial Coulombic efficiency (ICE) for the studied samples are given in Table 3. The discharge capacities of the LMNO-1 and LMNO-2 samples were 127 and 120 mAhg⁻¹, respectively. The two synthetized samples showed an increase of the discharge capacity and ICE compared with the commercial one.

However, LMNO-1 sample shows a higher decrease at the discharge capacity after 3 cycles. This degradation is greater than for the LMNO-2 and the commercial one.

The fast degradation of the LMNO-1 sample after 3 cycles should be due to the lack of Mn substitute by Ni as shown by Raman, ICP and XPS results. Those of this analysis showed that the LMNO-1 sample has a higher amount of Mn in comparison with the LMNO-2 and commercial sample.

The charge-discharge curves of the synthetized and commercial samples exhibited voltage plateaus at around 4.7 V due Ni²⁺/Ni⁴⁺ redox couple, and another one at about at 4.0 V due Mn³⁺/Mn⁴⁺ redox
Table 1. Atomic concentration obtained by XPS results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Li 1s</th>
<th>C 1s</th>
<th>O 1s</th>
<th>Mn 2p</th>
<th>Ni 2p</th>
<th>Atomic Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>LMNO-Commercial</td>
<td>3.59</td>
<td>9.08</td>
<td>51.25</td>
<td>27.61</td>
<td>8.47</td>
<td>0.42 3.26</td>
</tr>
<tr>
<td>LMNO-1</td>
<td>6.7</td>
<td>10.15</td>
<td>53.21</td>
<td>24.77</td>
<td>5.16</td>
<td>1.29 4.80</td>
</tr>
<tr>
<td>LMNO-2</td>
<td>7.66</td>
<td>7.82</td>
<td>53.00</td>
<td>25.69</td>
<td>5.84</td>
<td>1.31 4.40</td>
</tr>
</tbody>
</table>

Table 2. Composition of active material by Inductively Coupled Plasma (ICP)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition (wt %)</th>
<th>Molar Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li</td>
<td>Ni</td>
</tr>
<tr>
<td>LMNO-Commercial</td>
<td>3.77</td>
<td>16.1</td>
</tr>
<tr>
<td>LMNO-1</td>
<td>3.85</td>
<td>13.4</td>
</tr>
<tr>
<td>LMNO-2</td>
<td>3.76</td>
<td>15.6</td>
</tr>
<tr>
<td>LMNO-Commercial</td>
<td>3.80</td>
<td>16.06</td>
</tr>
</tbody>
</table>

*theoretical formulation of LiNi_{0.5}Mn_{1.5}O_4
Fig. 5 Charge-discharge curves of the active materials for the first three cycles, (a) LMNO-commercial (b) LNMO-1 (c) LNMO-2 at 0.3 C and operation voltage between 3.5 to 4.9 V
Table 3. Initial charge discharge capacities for the synthetized and commercial samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Charge / mAhg⁻¹</th>
<th>Discharge / mAhg⁻¹</th>
<th>ICE a / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>LMNO-Commercial</td>
<td>134</td>
<td>111</td>
<td>82.8</td>
</tr>
<tr>
<td>LMNO-1</td>
<td>146</td>
<td>127</td>
<td>87.0</td>
</tr>
<tr>
<td>LMNO-2</td>
<td>138</td>
<td>120</td>
<td>87.0</td>
</tr>
</tbody>
</table>

a initial Coulombic efficiency
couple. [18] Voltage plateau at around 4.7 V consist two voltage plateaus and they are attributed to the LiNi_{0.5}Mn_{1.5}O_{4} the spinel with structure Fd3m. [19] The plateau behavior at 4.0V varies strongly of the sample and it looks that it behavior affects greatly the degradation and cycle life of the cell.

As all the results showed, the sample synthetized with higher amount of Mn/Ni (LMNO-1) showed a high first discharge capacity and higher ICE but a shorter plateau at 4.6 V. This sample degrades faster than the synthetized with higher amount of Ni (LMNO-2), indicating that a lack of Ni substitution of Mn instead of Ni is presented at the spinel lattice and affecting the Ni^{2+}/Ni^{4+} redox couple and therefore more significant Jahn-Teller effect.

2.1.4 Conclusions

Two cathode active materials of LiNi_{0.5}Mn_{1.5}O_{4} were synthetized by a simple wet chemical reaction using acetate precursors. The synthetized products have spinel structure with space group of Fd3m, high crystallinity and uniform particle sizes and good electrochemical performance. The synthetized product showed obvious two discharge voltage plateau in comparison with the commercial one.

The sample synthetized with a higher Mn/Ni ratio shows a higher initial discharge capacity but a fast degradation behavior due to the lack of stability of Mn substitution by Ni and therefore more significant Jahn-Teller effect. The Ni redox reaction is affected as is shown by the difference of
behavior of two voltage plateau.

2.1.5 References


Chapter 3

Application to liquid phase heterogeneous oxidation catalyst

3.1 Creation of High-Valent Manganese Species on Hydrotalcite and Its Application to Catalytic Aerobic Oxidation of Alcohols

3.1.1 Introduction

The oxidation of alcohols is currently a significant issue in many important fields such as organic synthesis, hydrogen-storage/release, and transformation of renewable biomass resources. [1-2] For this purpose, manganese (Mn) compounds have long been used as oxidizing reagents due to their high oxidation ability. [3-5] While these compounds are extremely useful, stoichiometric amounts are necessary to achieve the oxidations, which results in vast amounts of irreversible Mn compounds as waste. From environmental and practical standpoints, these stoichiometric methods should be replaced by catalytic ones. Recently, several successful catalytic approaches using various kinds of oxidizing reagents have been reported. [6-8] Among these systems, a methodology using the green oxidant of molecular oxygen (O₂) as a reoxidizing reagent would be the most attractive approach leading to a minimum amount of waste. However, there are few reports on the construction of a catalytic cycle involving Mn species combined with O₂ for oxidation of alcohols. [9-11] Hydrotalcite [HT; Mg₆Al₂(OH)₁₆CO₃] is a layered anionic clay consisting of positively charged two-dimensional brucite layers with anionic species such as hydroxide and carbonate located in the interlayer. It has attracted considerable interest as a catalyst because of its multifunction potential due to its alternating cationic and anionic layers, surface tunable basicity, and metal-adsorption capacity. The metal-adsorption ability of HT offers strong potential to create various metal species on the surface. Immobilized metals on HT can act as efficient heterogeneous catalysts for various organic reactions. [12-15] Herein, a high-valent Mn oxide species (Mn/HT-Oₓ) was successfully
synthesized on the surface of HT, and found to oxidize alcohols. Interestingly, the resulting reduced Mn compounds could be reversibly reoxidized by O₂, and Mn/HT-Ox was applicable for the efficient aerobic oxidation of alcohols as a heterogeneous catalyst.

3.1.2 Experimental

General

All organic reagents were purified before use. [16] MnCl₂-4H₂O was purchased from Wako Pure Chemical Co., Ltd. as special grade, and used as received. MnO, Mn₂O₃, and MnO₂ were purchased from Merck Chemical Industries Co., Ltd. as reference compounds. Gas chromatography (GC-FID) was carried out on a Shimadzu GC-2014 equipped with a KOCL-3000T column (2 m). X-ray diffraction (XRD) was measured with an X’pert diffraction meter (Phillips Co., Ltd.).

Stoichiometric reaction of benzyl alcohol using Mn/HT-Ox

Mn/HT-Ox (0.6 g, Mn: 0.18 mmol) was placed in a reaction vessel equipped with a reflux condenser, followed by addition of degassed toluene (8 mL) and benzyl alcohol (1) (0.21 mmol). The reaction mixture was vigorously stirred at 100 °C under an inert atmosphere of Ar for 12 h in a glove box.

A typical procedure for the oxidation of 1 by Mn/HT-Ox

Mn/HT-Ox (0.2 g, Mn: 0.06 mmol) was placed in a reaction vessel equipped with a reflux condenser, followed by addition of toluene (8 mL) and 1 (1 mmol). After the reaction mixture was vigorously stirred at 100 °C under atmospheric pressure of O₂ for 12 h, Mn/HT-Ox was removed by centrifugation and the yield was determined by GC analysis with biphenyl as an internal standard.

X-ray Absorption Fine Structure (XAFS) Measurements

The Mn K-edge X-ray absorption data were recorded at room temperature in transmission mode at the facilities installed on the BL-01B1 line of SPring-8, Japan Atomic Energy Research Institute
(JASRI), Harima, Japan, using a Si(111) monochromator (proposal number: 2009B1506). The ordinate scale of the XANES spectra was normalized at 500 eV above the adsorption edge, where the differences in the XAFS oscillations among the spectra were negligible. The Mn K-edge position was taken as the first major peak in the corresponding derivative XANES spectrum. The XAFS data were normalized by fitting the background absorption coefficient around the energy region higher than the edge about 35-50 eV with the smoothed absorption of an isolated atom. Fourier transformation (FT) of $k^3$-weighted normalized XAFS data was performed over the $3.0 \, < \, k/\text{Å} \, < \, 12$ range to obtain the radial structure function. CN (the coordination number of scatterers), $R$ (the distance between an absorbing atom and scatterer), and Debye-Waller factor were estimated by curve-fitting analysis with an inverse FT assuming a single scattering. The structural parameters were determined by curve-fitting procedures with RIGAKU REX2000 ver. 2.5.7 data analysis software.

### 3.1.3 Results and Discussion

HT was synthesized according to the literature procedure. [18] HT was added to 50 mL of a $3.0 \times 10^{-4}$ M aqueous solution of MnCl$_2$·4H$_2$O, and then the heterogeneous mixture was stirred at 40 °C for 1 h under air, affording HT-containing Mn species (Mn/HT). Next, the pH of the solution was adjusted to 12 by adding 5 mL of an aqueous solution of KOH (1.0 M), and the resulting slurry was further stirred for 1 h. Finally, the obtained solid was isolated by filtration, washed with deionized water until the filtrate changed to neutrality, and dried at room temperature in vacuo, yielding Mn/HT-Ox as a brown powder. Elemental analysis of Mn/HT-Ox showed that the chemical composition of the Mn species was 1.6 wt%, and potassium ions were not detected. The XRD pattern of Mn/HT-Ox was similar to that of the parent HT.

Oxidation states of Mn/HT and Mn/HT-Ox were investigated using X-ray absorption fine
structure (XAFS) analysis comparing with reference Mn compounds of Mn foil, MnO, Mn$_2$O$_3$ and MnO$_2$. [19-21] The results are summarized in Fig. 1. The energy shift of the edge in X-ray absorption near-edge structure (XANES) indicated the average oxidation state of the Mn species in Mn/HT was 3.1 (Fig. 2, closed blue triangle). On the other hand, Mn in Mn/HT-Ox was oxidized up to a valency of 6 (Fig. 2, closed green circle).

Extended X-ray absorption fine structure (EXAFS) studies showed that Mn/HT-Ox had no peak at 1.9 Å from a Mn-O shell which appeared in Mn/HT, and the magnitudes of two prominent peaks attributed to Mn–O and Mn–Mn shells around 1-3 Å in Mn/HT-Ox were greater than those in Mn/HT (Fig. 3). The inverse FT of these two peaks around 1–3 Å was well fitted using a Mn–O bond (1.9 Å) and a Mn–Mn bond (2.9 Å) with coordination numbers (CN) of 6.0 and 3.6, respectively. The above results suggest that highly dispersed planar manganese oxide clusters consisting of approximately seven Mn atoms are formed on the surface of Mn/HT-Ox (Table 1).

These results reveal that adding KOH raises the oxidation state of the Mn species on HT to afford the high-valent Mn species. It is said that base compounds are effective additives for the formation of stable high-valent Mn species. [22, 23] Both KOH and the surface basicity of HT may stabilize the high-valent Mn species generated on HT.

Mn/HT and Mn/HT-Ox were treated with 1 in toluene at 100 °C under Ar atmosphere. Mn/HT-Ox could oxidize 1 to give benzaldehyde (2) stoichiometrically, together with the formation of a reduced Mn/HT-Ox (Fig. 2, open green circle and Fig. 4b), while Mn/HT resulted in an extremely low yield of 2. Notably, when the reduced Mn/HT-Ox was treated under an air atmosphere, the reduced Mn species was easily reoxidized to the original high-valent Mn species (Fig. 2, closed red square and Fig. 4c). Moreover, the regenerated high-valent Mn species on Mn/HT-Ox could oxidize 1 again, affording 2 and the reduced Mn species (Fig. 2, open red square and Fig. 4d). These phenomena indicate that the high-valent Mn species on the HT surface can oxidize 1, and then, reduced
Mn/HT-Ox can be reoxidized by O$_2$ reversibly. The redox property of Mn/HT-Ox during the above treatment was also confirmed by EXAFS analysis: the peak intensity of Mn-O in FT increased then decreased when treatment with O$_2$ followed by 1 was conducted (Fig. 3).

In addition to XAFS analysis, XRD and XPS measurement were employed to characterize the bulk structure and the oxidation state of manganese oxide. From the result of XRD measurement (Fig. 5), the spectra of Mn/HT exhibited small peak around $2\theta = 32$ assigned to Mn$_3$O$_4$. [24-26] This peak was disappeared by KOH treatment as the spectra of Mn/HT-Ox could be seen and the crystal geometry was reconstructed to uniform layered structure.

X-ray photoelectron spectroscopy (XPS) measurements were performed to evaluate the oxidation state of Mn/HT-Ox and authentic $\beta$-MnO$_2$ oxide. (Fig. 6) For Mn/HT-Ox, the Mn2p $3/2$ band shows the peak position at 646.5 eV. The change of binding energy between Mn/HT-Ox and MnO$_2$ indicates that the average oxidation state of manganese in Mn/HT-Ox increased by KOH treatment. These results supported the XANES and EXAFS studies.

Encouraged by the above results, the author next investigated the catalytic potential of Mn/HT-Ox for the aerobic oxidation of 1. To evaluate the catalytic properties of the Mn/HT-Ox, the oxidation of 1 was carried out using various manganese catalysts under an atmospheric pressure of O$_2$, and the results are listed in Table 2. Among the hydrotalcite, hydrotalcite-immobilized Mn catalysts, other oxides-immobilized Mn catalysts and manganese oxides, the Mn/HT-Ox exhibited the highest catalytic activity for the oxidation of 1 to give 2. In the cases of the Mn/HT catalysts, the conversion of 1 was low to give only 20% yield as a product. Other Mn immobilized catalysts scarcely converted to give 2. Various manganese oxides are also ineffective for this oxidation. It is said that stoichiometric amounts of manganese oxides are necessary to achieve the oxidations. [3-5]

Obviously, the high valent Mn species acts as catalytically active sites for this alcohol oxidation and the hydrotalcite plays an essential role as support in this catalyst system. Using the hydrotalcite
Fig. 1 Mn K-edge XANES spectra of (a) Mn foil, (b) MnO, (c) Mn$_2$O$_3$, (d) beta-MnO$_2$, (e) KMnO$_4$, (f) Mn/HT and (g) Mn/HT-O$\alpha$. 
Fig. 2  Mn valence vs Mn K-edge position of experimental samples for reference Mn model compounds.
Fig. 3  Fourier transformation (FT) of the $k^3$-weighted K-edge EXAFS spectrum of (a) Mn/HT, (b) Mn/HT-Ox, (c) reduced Mn/HT-Ox with alcohol under Ar, (d) re-oxidized Mn/HT-Ox under air, and (e) reduced Mn/HT-Ox with alcohol under Ar after re-oxidation.

Table 1 Results of Curve-Fitting Analysis of Mn/HT-Ox

<table>
<thead>
<tr>
<th>shell</th>
<th>CN$^a$</th>
<th>R/Å$^b$</th>
<th>σc / Å$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn-O</td>
<td>6.065</td>
<td>1.905</td>
<td>0.0081</td>
</tr>
<tr>
<td>Mn-Mn</td>
<td>3.611</td>
<td>2.913</td>
<td>0.0021</td>
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</table>

$^a$ Coordination number. $^b$ Interatomic distance. $^c$ Difference between Debye-Waller factor of Mn/HT-Ox and that of the reference sample.
Fig. 4  Mn K-edge XANES spectra for the redox experiments. (a) Mn/HT-Ox, (b) after reduction of Mn/HT-Ox with alcohol under Ar, (c) re-oxidation of reduced Mn/HT-Ox under air and (d) reduction of re-oxidized Mn/HT-Ox under same condition of (b).
Fig. 5 XRD Patterns of Hydrotalcite and Mn-immobilized Hydrotalcites
Fig. 6 C1s and Mn 2p XPS spectra for MnO$_2$ and Mn/HT-Ox
without Mn component, the oxidation of 1 did not proceeded.

Subsequently, the catalytic potential of Mn/HT-Ox for various alcohols was examined. Mn/HT-Ox showed a highly catalytic activity for the oxidation of benzylic alcohols under an atmospheric pressure of O₂ (Table 1, entries 1, 5-13). For example, various benzylic alcohols with functional groups such as chlorine, nitro, and methyl at para positions were converted to the corresponding aldehydes in excellent yields (entries 7-10). Heterocyclic alcohols also exhibited high reactivities (entries 11 and 12). In addition, cinnamyl alcohol gave the corresponding cinnamaldehyde as the sole product, while the C=C double bond was not affected by the reaction. Aliphatic and allylic alcohols such as 2-octanol and geraniol gave low yields of products (entries 14 and 15). The obtained results reveal that Mn/HT-Ox shows high catalytic activity for benzylic and cinnamyl alcohols, and low activity for aliphatic alcohols. The above substrate scope of Mn/HT-Ox is similar to those of stoichiometric Mn reagents such as BaMnO₄ and active MnO₂. [27, 28] The addition of radical scavengers of galvinoxyl, 4-tert-butylcatechol, and N-tert-butyl-α-phenylnitrone in the identified reaction conditions inhibited the oxidation, suggesting that this Mn/HT-Ox-catalyzed oxidation involves the radical path. It is said that stoichiometric amount of MnO₂ is also radical path. [28, 29] On the basis of the stoichiometric oxidation of alcohols using Mn compounds proposed by Goldman, the author proposed a plausible reaction path as shown in scheme1.

The great advantage of our newly developed Mn/HT-Ox is that catalytic amounts of Mn are sufficient to achieve the oxidation while the conventional Mn reagents are needed in more than stoichiometric amounts. Because of the heterogeneous character of the present oxidation, the Mn/HT-Ox catalyst was readily separated from the reaction mixture by simple filtration. In the aerobic oxidation of 1, the recovered catalyst could be reused without any appreciable loss of its high activity or selectivity in three times recycling experiments (Table 1, entries 2-4). During the
above recycles, no leaching of Mn species in the filtrate was detected by an ICP method whose detection limit was 24 ppb. To confirm whether the oxidation of alcohol occurred at the Mn species on the hydrotalcite solid, the Mn/HT-Ox, in the case of the aerobic oxidation of benzyl alcohol, was removed by filtration after ca. 50% conversion of benzyl alcohol at the reaction temperature. Further treatment of the filtrate under similar reaction conditions did not afford any product. (Fig.8) In addition, the recovered catalyst maintained its original high-valent Mn structure, as confirmed by XAFS.

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>conv. (%)</th>
<th>yield (%)</th>
</tr>
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<tr>
<td>1</td>
<td>Mn/HT-Ox</td>
<td>&gt;99</td>
<td>&gt;99</td>
</tr>
<tr>
<td>2</td>
<td>Mn/HT</td>
<td>23</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>Mn/HT</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>Mn/MgO</td>
<td>9</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>Mn/Al₂O₃</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>MnO₂</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>7</td>
<td>Mn₂O₃</td>
<td>N.R.</td>
<td>N.R.</td>
</tr>
<tr>
<td>8</td>
<td>MnO</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>9</td>
<td>MnO₂+HT</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>10</td>
<td>HT</td>
<td>N.R.</td>
<td>N.R.</td>
</tr>
</tbody>
</table>

Table 2  Effect of various manganese compounds for the Aerobic Oxidation of Benzyl Alcohol

- Reaction conditions: Benzyl Alcohol 1mmol; catalyst Mn:6mol%; toluene 8ml;O₂ atmosphere; time 12h; temperature 100° C. 
- before base treatment. 
- precursor Mn(H₂PO₄)₂ oxidation state was determined by XANES. 
- Base treatment before reaction. 
- Reaction time; 15h.
Table 3  Aerobic oxidations of alcohols by Mn/HT-Ox Catalyst$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Time(h)</th>
<th>Conv.(%)$^b$</th>
<th>Yield(%)$^b$</th>
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<tbody>
<tr>
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<tr>
<td>2$^c$</td>
<td></td>
<td></td>
<td>12</td>
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<td>99</td>
</tr>
<tr>
<td>3$^d$</td>
<td></td>
<td></td>
<td>12</td>
<td>97</td>
<td>97</td>
</tr>
<tr>
<td>4$^e$</td>
<td></td>
<td></td>
<td>12</td>
<td>99</td>
<td>99</td>
</tr>
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<td>5</td>
<td></td>
<td></td>
<td>11</td>
<td>&gt;99</td>
<td>&gt;99</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td>10</td>
<td>&gt;99</td>
<td>98</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td>11</td>
<td>&gt;99</td>
<td>&gt;99</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
<td>16</td>
<td>&gt;99</td>
<td>98</td>
</tr>
<tr>
<td>9</td>
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<td>15</td>
<td></td>
<td></td>
<td>24</td>
<td>11</td>
<td>10</td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: Substrate 1 mmol, Catalyst 6 mol%, toluene 5 ml, O$_2$ atmosphere, temperature 100 °C. $^b$Determined by GC using an internal standard technique. $^c$Cycle1. $^d$Cycle 2.$^e$Cycle 3.
Fig. 7 Effect of radical scavengers for the aerobic oxidation of 1 catalyzed by Mn/HT-Ox

Fig. 8 Leaching Test for the Reaction of Benzyl Alcohol Catalyzed by Hydrotalcites
Scheme 1 A plausible reaction path
3.1.4 Conclusion

In conclusion, high-valent Mn species could be created on the HT surface by treatment with KOH. The Mn compounds, which possessed redox properties with the combination of alcohol and molecular oxygen, could act as efficient heterogeneous catalysts for the aerobic oxidation of various benzylic alcohols. The present preparation method is a powerful protocol for the creation of high-valent Mn species on the surface of inorganic materials. The high-valent Mn species may catalyze other versatile oxidations.

3.1.5 References


3.2 Preparation of a zeolite X-encapsulated copper(II) chloride complex and its catalysis for liquid-phase oxygenation of enamines in the presence of molecular oxygen

3.2.1 Introduction

Highly selective transformation of organic compounds catalyzed by solid materials can contribute to the strong demand of environmental concerns in chemical processes because of the following advantages: (i) simple work-up procedures, (ii) reusable catalysts, and (iii) high thermal stabilities. [1–9] Use of metal catalysts in a liquid phase, however, sometimes leads to leaching of the active species from the solid surface into solution [10] which causes a serious loss of activity and contamination of the products. Here, the author describe the synthesis of a Cu(II) chloride complex catalyst within the pores of zeolite X for the selective oxygenation of enamines in the presence of molecular oxygen (Scheme 1). This catalyst can be reused without leaching of the Cu species and retains its high catalytic activity and selectivity for the above oxygenation.

\[ \begin{array}{c}
  \text{R}^1 \text{C}^\equiv \text{C}^\equiv \text{N}^\equiv \text{R}^3 \\
  \text{acetonitrile-DCE} \\
  50 \, ^{\circ}\text{C} \\
  \text{O}_2, \text{Cu-X zeolite} \\
  \end{array} \rightarrow \begin{array}{c}
  \text{R}^1 \text{C}^\equiv \text{O} \\
  + \text{O} \equiv \text{N} \equiv \text{R}^3 \\
  \text{R}^4 \\
  \end{array} \]

Scheme 1
3.2.2 Experimental

Preparation

Copper ion-exchanged X zeolite (Cu–X) was prepared by a treatment of Na–X zeolite, \( \text{Na}_{86}(\text{Al}_{86}\text{Si}_{106}\text{O}_{384})\cdot264\text{H}_2\text{O} \) (Si/Al = 1.23, Wako Co. Ltd.), with a 0.01 M aqueous solution of Cu(NO\(_3\))\(_2\)·3H\(_2\)O. The powder was washed with deionized water, followed by drying and calcination at 300 °C to give a sky-blue Cu–X sample. The Cu content in this sample was 12.0 wt%, which corresponds to 83% ion exchange degree of Na\(^+\).

A typical procedure for the oxidation of enamine by Cu-X

Cu-X was placed in a reaction vessel equipped with a reflux condenser, followed by addition of acetonitrile (7 ml) and 1,2-dichloroethane (1 mL) and substrate (1 mmol). After the reaction mixture was vigorously stirred at 50 °C under atmospheric pressure of O\(_2\) for 5 h, Cu-X was removed by centrifugation and the yield was determined by GC analysis with biphenyl as an internal standard.

3.2.3 Results and Discussion

Retention of the crystal structure of the X zeolite was confirmed by XRD. In situ EPR, UV–VIS and Cu K-edge XANES spectra for the Cu–X sample indicated dispersed divalent Cu\(^{2+}\) with a centrosymmetric coordination environment, \textit{i.e.} octahedral.

Curve-fitting analysis of the Fourier-transformed copper EXAFS showed that the Cu\(^{2+}\) cations displayed Jahn–Teller distorted CuO\(_6\) octahedra \cite{11} with four short Cu–O distances (1.91 Å) and two long Cu–O distances (2.28 Å). The Cu–O distance of 1.91 Å is slightly shorter than the value of 1.97 Å found in Cu–Y zeolites. \cite{12} A lack of a peak at \textit{ca.} 3 Å in the Fourier transform of the Cu K-edge EXAFS indicated selective formation of monomeric Cu\(^{2+}\) species. A coordination sphere of the CuO\(_6\) octahedra within the zeolite pores is proposed as shown in Fig. 1(a) where the Cu\(^{2+}\) ion is...
Fig. 1 Proposed schematic structure of Cu$^{2+}$ octahedral species within the framework structure of zeolite X. (a) CuO$_6$ octahedral species, (b) CuO$_4$Cl$_2$ octahedral species. The octahedral CuO$_4$X$_2$ species is coordinated to oxygens of zeolite framework and H$_2$O ligands. The positions of exchangeable cations are indicated Roman letters.
reasonably located in a vicinity of the exchangeable site II, just outside the sodalite cage in a large pore with 7.4 Å diameter. [13, 14] Cu–X (0.50 g) was further treated with 1,2-dichloroethane (DCE, 10 mL) at 50 ºC for 1 h, followed by drying to afford an emerald greenish powder, Cu(Cl)–X. The presence of Cu–Cl bonds was confirmed by XPS measurements and elemental analysis; the atomic ratio of Cu to Cl was 1 : 1.8. EXAFS analysis of Cu(Cl)–X also revealed a Jahn–Teller distorted Cu$^{2+}$ octahedron with four Cu–O bonds (1.92 Å) and two Cu–Cl bonds (2.29 Å). The Cu–Cl distance of 2.29 Å is consistent with a Cu–Cl bond length of 2.30 Å in CuCl$_2$ and a proposed structure of the monomeric Cu$^{2+}$ chloride complex is shown in Fig. 1(b). To our knowledge, this is the first example of the synthesis of a copper(II) chloride species within a pore of zeolite X. It has been stated that Cu chloride complexes can not be formed within the pores of zeolite X by a simple exchange reaction of Na–X with CuCl$_2$ solution because of destruction of the faujasite structure of zeolite X. [15] In zeolite Y, adoption of burdensome methods such as chemical vapor deposition [12] or a solid-state ion-exchange [15] can afford monovalent copper chloride species. The chlorine in Cu(Cl)–X originates from a DCE molecule during the treatment of Cu–X with DCE. The fact is supported by the formation of dibenzyl ether upon treatment of Cu–X with benzyl chloride in place of DCE. [16]

It has been already reported by the author’s group that copper chloride compounds are effective homogeneous catalysts for the oxidative cleavage of carbon double bonds of enamines in the presence of molecular oxygen. [17, 18] To explore the potential catalytic abilities of the Cu(II) chloride complexes within the zeolite X, [19-21] oxygenation of enamines using Cu–X was performed. The order of the catalytic activity of various copper catalysts for the oxygenation of 1-(4-morpholino)-2-methylpropene is:

Cu–X (93) > Cu–Y (82) > Cu-mordenite (76) > Cu/Al$_2$O$_3$ (72) > Cu/SiO$_2$ (38),

where values in parentheses are yields of N-formylmorpholine. Typical results for the oxygenation
of enamines with Cu–X in acetonitrile–DCE are summarized in Table 1. The author confirmed that the catalysis of Cu–X in the mixed solvent corresponded to that of Cu(Cl)–X. Cu(Cl)–X itself effectively oxygenated the enamine in acetonitrile alone (yield: 70%). Solvents having high dielectronic constants such as acetonitrile, DMF and ethanol were effective co-solvents for DCE, as similarly observed in the homogeneous catalyst system using CuCl$_2$. [17, 18] The carbon double bonds of many enamines were smoothly cleaved to give the corresponding amides and ketones (entries 1, 2 and 4–8). For a bulky enamine such as 1-(4-morpholino)-2,2-diphenylethene, the oxygenation rate with Cu–X was slower than that of a homogeneous CuCl$_2$ catalyst (entry 9 vs. 10). This different activity between the heterogeneous Cu–X and the homogeneous CuCl$_2$ catalyst might be ascribed to a shape-selective effect of Cu$^{2+}$ species within the three-dimensional zeolite pores. The Cu–X catalyst was also active for the oxygenation of 2,3-dimethylindole (entry 11). Interestingly, this heterogeneous catalyst showed higher activity than CuCl$_2$ for 2,3-dimethylindole, [22, 23] however, the oxidation of 3-methylindole resulted in a low yield (34% after 24 h).

The Cu–X catalyst could be easily separated from the reaction mixture and reused without an appreciable loss of its activity for the oxygenation; the first, second and third runs of the reused catalyst for 1-(4-morpholino)-2-methylpropene gave N-formylmorpholine in > 90% yield. The loss of Cu content in the spent Cu–X catalyst after several reuse experiments was < 1%; the Cu content in the catalyst did not change even after the third reuse. ICP analysis of copper in the liquid phase after oxygenation showed that leached copper from the catalyst was < 1% in the spent Cu–X catalyst. When the filtrate at 50% enamine conversion was allowed to react further at 50 °C under an oxygen atmosphere, oxygenation did not occur. The fact that the active copper complex does not leach from the zeolite X during the oxygenation and recycling procedures, indicates a reusable heterogeneous catalyst for the liquid-phase oxidation.

It is presumed that the oxygenation catalysed by the Cu(Cl)–X catalyst might involve
one-electron transfer from the enamine to molecular oxygen in a ternary Cu$^{2+}$ complex bonded to enamine and O$_2$, followed by the formation of Cu$^{2+}$ and a dioxetane intermediate. [17, 18] Strong binding of the Cu chloride complexes on the zeolite is due to the location of the divalent Cu ions within large supercages, bound to oxygens of the zeolite framework [Fig. 1(b)]. [24] During the oxygenation, facile coordination of enamine and O$_2$ to the active Cu center can occur since some ligands such as H$_2$O on the Cu active species are labile.
### Table 1. The oxidative cleavage of enamines catalyzed by Cu-X zeolite in the presence of molecular oxygen$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Time (h)</th>
<th>Conv. (%)</th>
<th>Yield (%)$^b$</th>
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<th></th>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Amide</td>
<td>Ketone</td>
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<td>97</td>
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<tr>
<td></td>
<td></td>
<td>5</td>
<td>98</td>
<td>90 (reuse-1)</td>
<td>c</td>
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<td></td>
<td></td>
<td>5</td>
<td>98</td>
<td>90 (reuse-3)</td>
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<td>3</td>
<td>&gt;99</td>
<td>84$^e$</td>
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</table>

$^a$ Reaction conditions: Substrate (1 mmol), Cu-X (0.10 g, 0.19 mmol as Cu), solvent (8 mL; acetonitrile - DCE, 7:1), O$_2$ atmosphere, 50 °C. $^b$ Yields based on enamine. $^c$ Acetone formed, however, the yields were not determined. $^d$ Homogeneous oxidation using CuCl$_2$ (0.19 mmol). $^e$ N-(2-Acetylphenyl)acetamide isolated by column chromatography on silica gel.
3.2.4 Conclusion

In conclusion, monomeric copper(II) chloride species within the pore of zeolite X can be synthesized by a novel and convenient method, and are found to be effective catalysts for the cleavage of enamine double bonds in the presence of molecular oxygen. This zeolite X-encapsulated copper chloride complex is a unique instance of a heterogeneous and reusable catalyst which does not undergo leaching of the activespecies.

3.2.5 References


Chapter 4

Application to gas phase heterogeneous catalyst

4.1 Preparation of Highly Dispersed Cu Species on TiO₂ Using Cu(II) Complexes

4.1.1 Introduction

TiO₂-supported Cu shows a catalytic activity for methanol reforming, [1] NO and N₂O decomposition, [2-5] combustion of soot particles, [6] etc. For these reaction systems, it is summarized that reduced Cu ions, e.g., Cu⁺ and Cu⁰, act as the active center, and the support-interaction between Cu and TiO₂ is very effective for stabilizing reduced Cu species. However, formation of highly dispersed Cu species on the support-oxide is difficult because Cu ions tend to aggregate to form Cu-cluster species by means of general preparation method. In the case of Cu ionexchanged zeolites such as Cu-ZSM-5 and Cu-Y, Cu ions can be stabilized in the channel of frameworks dispersively, and well-dispersed Cu ions can be obtained. [7-10] These Cu ions show a high catalytic activity for deNOx reactions because Cu ions can easily be reduced thermally. [11] In the case of cupric nitrate precursor, almost Cu²⁺ ion could not be reduced, because Cu²⁺ cluster was formed. Since strong cation exchange site does not exist on the oxide supports used widely (such as TiO₂, ZrO₂, ZnO, SiO₂, etc.), the preparation of highly dispersed Cu ions on the support is necessary to obtain a novel catalyst exhibiting high redox activity.

In this chapter, the author attempted to prepare highly dispersed Cu ions on TiO₂ support. It is reported that highly dispersed NbOx species are formed on TiO₂ by using Nb⁵⁺ complex [Nb(dbm)₄Cl⁻, Hdbm : 1,3-diphenyl-1,3-propanedione]. [12] By use of Cu²⁺ complex with bulky ligands, dispersion of Cu ions can be expected. Two Cu²⁺ complexes were employed in preparing Cu/TiO₂ to form isolated Cu²⁺ species on TiO₂. The state of Cu ions and their behavior of thermal reduction were appreciated by means of ESR spectroscopy.
4.1.2 Experimental

The Cu/TiO$_2$ samples were prepared by impregnation of ultra-fine TiO$_2$ particle (IT-S; Idemitsu Kosan Co., Ltd.) support which calcined at 600 °C for 6h with an aqueous solution of Cu(NO$_3$)$_2$·3H$_2$O or methyl chloride solution of Cu$^{2+}$ complexes. The synthesized complexes used in this study are bis-(acetylacetonato)-copper(II) [Cu(acac)$_2$] and bis-(1,3-diphenyl-1,3-propanedionato)-copper(II) [Cu(dbm)$_2$]. The Cu-loading is 0.1 wt% in all the samples. The impregnated samples were then dried at 120 °C for overnight and calcined at 600 °C for 3 h. In this paper, the samples prepared from Cu(NO$_3$)$_2$·3H$_2$O, Cu(acac)$_2$, and Cu(dbm)$_2$ were designated as Cu(N)/TiO$_2$, Cu(A)/TiO$_2$, and Cu(D)/TiO$_2$, respectively. All the samples consisted of anatase type TiO$_2$, because of calcined at 600 °C. Each sample (0.05 g) was set to the in situ quartz cell and evacuated at given temperature between 100 and 500 °C for 1 h prior to ESR measurement. ESR spectra (X-band) were recorded with JEOL JES-ME3X spectrometer at room temperature. The $g$-values and the signal intensity were evaluated by use of Mn$^{2+}$-marker as an internal standard and CuSO$_4$·5H$_2$O as a reference of Cu$^{2+}$ sample.

4.1.3 Results and Discussion

The surface areas of samples were increased with evacuated temperature from 45 to 60 m$^2$/g. For all Cu/TiO$_2$ samples after evacuation, ESR signal of Cu$^{2+}$ can be seen definitely at $g=2.040$ as a center. This Cu$^{2+}$ signal exhibits different intensity between the samples prepared. The relation between the evacuation temperature and signal intensity in Cu(N)/TiO$_2$, Cu(A)/TiO$_2$, and Cu(D)/TiO$_2$ is shown in Figure 1. In the case of low evacuation temperature at 100–300 °C, the intensity of Cu$^{2+}$ signal in Cu(N)/TiO$_2$ is lower than those in Cu(A) and Cu(D)/TiO$_2$. It can be explained that the loss of the signal intensity is due to the dipole-dipole interaction of Cu$^{2+}$ clusters. Thus, the Cu ions in Cu(N)/TiO$_2$ contain aggregated Cu$^{2+}$ cluster species. It supports the several
Fig. 1 Relation between the intensity of Cu²⁺ ESR signal and evacuated temperature (equimolecular CuSO₄·5H₂O as a reference of Cu²⁺)
works that Cu ions on TiO$_2$ tend to aggregate by use of cupric nitrate as a precursor. [1, 13, 14] For Cu(A)/TiO$_2$ and Cu(D)/TiO$_2$, about 83% of Cu$^{2+}$ is ESR-visible even after evacuation at 100 °C. In these samples, more than 90% of Cu$^{2+}$ can be seen after evacuation at room temperature. These results show that well dispersed Cu$^{2+}$ ions on TiO$_2$ are obtained by use of Cu$^{2+}$-complexes as a precursor. With an increase of evacuated temperature, Cu$^{2+}$ signal is reduced in all the samples. Since these samples were calcined sufficiently at 600 °C before evacuation, aggregation of Cu ions during the evacuation is not reasonable. The disappearance of the signal is assigned to the thermal reduction of Cu$^{2+}$ ions to form Cu$^+$. [15] In the case of Cu(N)/TiO$_2$, low evacuation temperature up to 300 °C, the slope of signal reduction is almost as similar as those in Cu(A)/TiO$_2$ and Cu(D)/TiO$_2$. However, it is remarkable that the slope becomes low above 300 °C. It is inferred that isolated Cu$^{2+}$ in Cu(N)/TiO$_2$ is reduced below 300 °C, and most of thermally reducible Cu$^{2+}$ ions are occupied by the ESR-inactive cluster species above 300 °C. It is reported that aggregated Cu$^{2+}$ cluster can hardly be reduced to Cu$^+$ below 500 °C,14 and thus, reduction of Cu$^{2+}$ in Cu(N)/TiO$_2$ may scarcely proceed at 300–500 °C. On the other hand, the signal intensity in Cu(A)/TiO$_2$ and Cu(D)/TiO$_2$ decreased monotonously with increasing of evacuation temperature up to 500 °C. It has been accepted that isolated Cu$^{3+}$ can easily be reduced thermally for Cu/SiO$_2$ and Cu ion-exchanged zeolites. [9, 16, 17] It is appropriate that Cu$^{2+}$ ions in Cu(A)/TiO$_2$ and Cu(D)/TiO$_2$ also be reduced thermally because of isolation of Cu ions. The difference of the slope between Cu(A)/TiO$_2$ and Cu(D)/TiO$_2$ is still unclear, however, it is likely that the molecular size of Cu(dbm)$_2$ is too large to exceed the full coverage of TiO$_2$ surface slightly.

4.1.4 Conclusion

In conclusion, highly dispersed Cu ions on TiO$_2$ can be prepared by use of Cu$^{2+}$ complexes as a precursor than that of Cu$^{3+}$ nitrite. The isolated Cu$^{2+}$ ions can be reduced thermally up to 500 °C.
**Scheme 1** Formation of surface structure of Cu(A) or Cu(D)/TiO$_2$ catalyst.

*The intramolecular inter-atom distances by model structures:
Each bond length between the neighbor atoms are 1.395 Å, and bond angles 120°.*
4.1.5 References


List of Publication

Chapter 1

Development trend of solid hydrogen source for fuel cell using calcium compounds
Kohji Nagashima, Hitoshi Ishizaka, Hiroshi Miura, Akira Kamisawa, and Kazuyuki Hirao


Solid hydrogen source for fuel cell
Kazuyuki Hirao, Kohji Nagashima, Heidy Visbal, Hitoshi Ishizaka, Hiroshi Miura, and Akira Kamisawa


Modification of Calcium Hydride for Solid Hydrogen Source Fuel Cell
Kohji Nagashima, Hitoshi Ishizaka, Akira Kamisawa, Heidy Visbal and Kazuyuki Hirao

To be published in *International Journal of Applied Ceramic Technology*

Controllable hydrogen release via aluminum powder corrosion in calcium hydroxide solutions
Shingo Kanehira, Susumu Kanamori, Kohji Nagashima, Takashi Saeki, Heidy Visbal, Toshimi Fukui, and Kazuyuki Hirao

Aluminum Corrosion Promotion by Calcium Hydroxide for Hydrogen Generation from Water
Kohji Nagashima, Shingo Kanehira, Masayuki Nishi, Masahiro Shimizu, and Kazuyuki Hirao

Design of controllable hydrogen generation system using Al foil
Kohji Nagashima, Heidy Visbal, Shingo Kanehira, Takashi Saeki, Ryosuke Chinzaka, Masahiro Shimizu, Masayuki Nishi, and Kazuyuki Hirao
To be submitted to International Journal of Hydrogen Energy

Study on long-term production of hydrogen by hydrolysis of Al foil in calcium hydroxide solution
Kohji Nagashima, Heidy Visbal, Shingo Kanehira, Takashi Saeki, Ryosuke Chinzaka, Masahiro Shimizu, Masayuki Nishi, and Kazuyuki Hirao
To be submitted to Journal of the American Ceramic Society

Surface Analysis of Three Different Aluminum Foils and Its Relation with Hydrogen Generation Capability
Heidy Visbal, Kohji Nagashima, and Kazuyuki Hirao
To be published in Korean Journal of Chemical Engineering
Chapter 2

Synthesis of spinel LiNi₀.₅Mn₁.₅O₄ by a wet chemical method and characterization for lithium-ion secondary batteries
Luz Quispe, Marco A. Condorett, Hideki Kawasaki, Seiji Tsuji, Heidy Visbal, Hitomi Miki, Kohji Nagashima, and Kazuyuki Hirao


Chapter 3

Creation of a high-valent manganese species on hydrotalcite and its application to the catalytic aerobic oxidation of alcohols
Kohji Nagashima, Takato Mitsudome, Tomoo Mizugaki, Koichiro Jitsukawa, and Kiyotomi Kaneda


Preparation of a zeolite X-encapsulated copper(II) chloride complex and its catalysis for liquid-phase oxygenation of enamines in the presence of molecular oxygen
Kohki Ebitani, Kohji Nagashima, Tomoo Mizugaki, and Kiyotomi Kaneda

Chemical Communications, pp.869-870 (2000)

Chapter 4

Preparation of highly dispersed Cu on TiO₂ using Cu(II) complexes
Kohji Nagashima, Hisao Kokusen, Norieda Ueno, Ayako Matsuyoshi, Tomomi Kosaka, Miki Hasegawa, Toshihiko Hoshi, Kohki Ebitani, Kiyotomi Kaneda, Hirofumi Aritani, and Sadao
Hasegawa

<Related Work>
Simple and clean synthesis of 9,9-bis[4-(2-hydroxyethoxy)phenyl]fluorene from the aromatic alkylation of phenoxyethanol with fluoren-9-one catalysed by titanium cation-exchanged montmorillonite
Kohki Ebitani, Tomonori Kawabata, Kohji Nagashima, Tomoo Mizugaki and Kiyotomi Kaneda

List of Patent

Chapter 1


<Related Work>
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