Recovery of Lithium from Geothermal Fluid at Lumpur Sidoarjo by Adsorption Method

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Abstract. The recovery of lithium from geothermal fluid at Lumpur Sidoarjo, Indonesia was investigated employing an adsorption method with polymer membrane as container. The lithium concentration in geothermal fluid from Lumpur Sidoarjo used in the present study was about 5 mg/l. Lithium manganese oxide (LMO) was selected as a promising adsorbent material due to its non-toxic, topotactical behavior and low cost. In this study, LMO with single Li/Mn mole ratio was prepared, i.e. $Li_{1.6}Mn_{1.6}O_4$. The adsorbent was synthesized by solid state reaction at 500 °C for 5 hrs. A lithium uptake yield from the geothermal fluid of around 6.6 mg/g was obtained.

Keywords: *geothermal fluid; lithium; lithium manganese oxide; Lumpur Sidoarjo; spinel.*

1 Introduction

Lithium is considered to be a rare mineral in Indonesia. Of all materials, lithium currently has the highest demand in the world because of the rapid development of portable electronic devices such as mobile phones, tablets and laptops. The rising interest in electric cars in the last few years also boosts the increasing consumption of lithium. The high demand for lithium is shown by the rate of lithium consumption in 2012, which industry analysts and lithium producers have estimated at 28,000 tons used throughout the year. This number was an increase of 10% compared to worldwide lithium consumption in 2011 [1].

Lithium in natural resources is found in several types, ranging from brine to minerals rock. Brine is the most commonly used because of its high lithium content, while spodumene is the mineral form of lithium. There are also alternative sources that are still being investigated, i.e. seawater and geothermal fluids. Both of these sources actually have less lithium content, but judging

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from the abundance and ease of the production process these two sources have great potential as alternative production sources of lithium.

Geothermal fluid can generally be interpreted as a fluid trapped inside the earth's crust. Due to heat and pressure this fluid reacts with surrounding minerals and rocks. Therefore, some geothermal fluids have a high content of minerals, especially lithium. A major site of geothermal fluid effusion in Indonesia is Lumpur Sidoarjo (Lusi), near Surabaya, East Java. Lusi is a phenomenon where there is high-temperature mud that flows continuously from the inside of the earth's crust. In 2011, the debit of the mud reached 10,000 m^3/day. This phenomenon is predicted to occur until approximately 25 years from now [2]. Several investigations of the lithium content in Lusi have been conducted by fellow researchers. Their results show that the lithium content reaches up to 5 ppm (mg/liter) [3]. On the basis of a rough calculation with the assumption that the discharge of mud and the lithium content are constant, Lusi has the ability to produce as much as 18 tons of lithium annually.

Some preliminary experiments have been conducted to find the best way to recover lithium from geothermal fluids. One way is by adsorption. This method is frequently used with sea water [4-6]. An inorganic adsorbent is used to adsorb lithium ions from the source. One of the adsorbent compounds is lithium manganese oxide (LMO) [7,8]. LMO has a crystal structure with different atomic configurations. The type of crystal structure has an effect on the lithium adsorption characteristics.

In this work, LMO with single Li/Mn mole ratio, i.e. $Li_{1.6}Mn_{1.6}O_4$, was synthesized using a solid-state reaction method. Lithium carbonate and manganese oxide were used as precursors [9,10]. Then, the crystal structure and the ability to adsorb lithium from Lusi of the as-prepared adsorbent were systematically studied.

2 Experimental procedures

Lithium manganese oxide ($Li_{1.6}Mn_{1.6}O_4$) was synthesized from $LiCO_3$ (ACS reagent, ≥ 99.0 %, Sigma-Aldrich) and MnO_2 (ACS reagent, ≥ 99.0%, Sigma-Aldrich) using a solid-state reaction method. The two reagents were dissolved and mixed well in ethanol. The mixture was calcined at 500 °C for 5 hours. After cooling to room temperature, the prepared LMO powders were dissolved in 0.5M HCl solution for 24 hours to elute the lithium and form a vacant site in the spinel structure of the LMO, producing an ion sieve type adsorbent to adsorb lithium ions from Lusi geothermal fluid.

The change of the spinel structure of the sample before and after the acid treatment was examined using X-ray diffraction (XRD, Philips Xpert with a Cu-Kα radiation tube), the morphology of the particles was observed using scanning electron microscopy (SEM, Philips FEI). The concentration of Li in the supernatant solution was determined through induced couple plasma (ICP) and the extractabilities of the metal ions were calculated accordingly.

Adsorbent preparation was started with cutting the sheet of polypropylene membrane (Kimtex®), which was subsequently filled with LMO powder as much as 0.1 grams. The adsorption properties of the LMO adsorbent were tested through various experiments with the Lusi geothermal fluid.

3 Results and Discussion

An SEM image of the prepared LMO is shown in Figure 1. It can be seen that the prepared LMO powders have particles sizes varying between 3 μm and 60 μm.

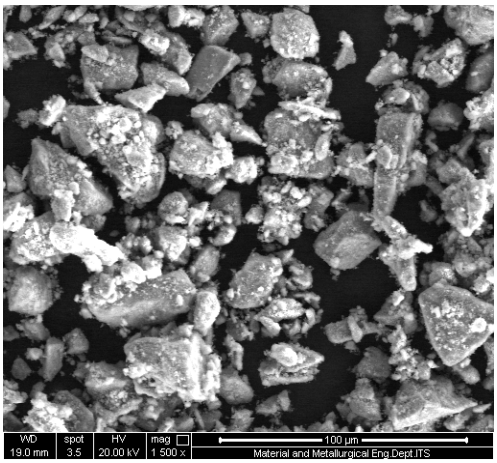

Figure 1 SEM image of LMO.

The XRD result of the LMO is shown in Figure 2. The XRD patterns could be indexed as LMO with spinel crystal structure as PDF Card 00 - 052-1841. No diffraction peaks of impurity were detected. In addition, the narrow peaks with strong intensity indicate that the as-prepared LMO had high crystallinity.

An XRD test was also performed after the acid treatment of the LMO adsorbent, as shown in Figure 3. Generally, the shape of the diffraction pattern of the LMO after the acid treatment was similar to the diffraction pattern before the acid treatment. However, the peaks after the acid treatment shifted toward the right

side of the diffraction pattern. This indicates that the acid treatment had no impact on the spinel structure of the LMO. This kind of stability is desired for application as adsorbent.

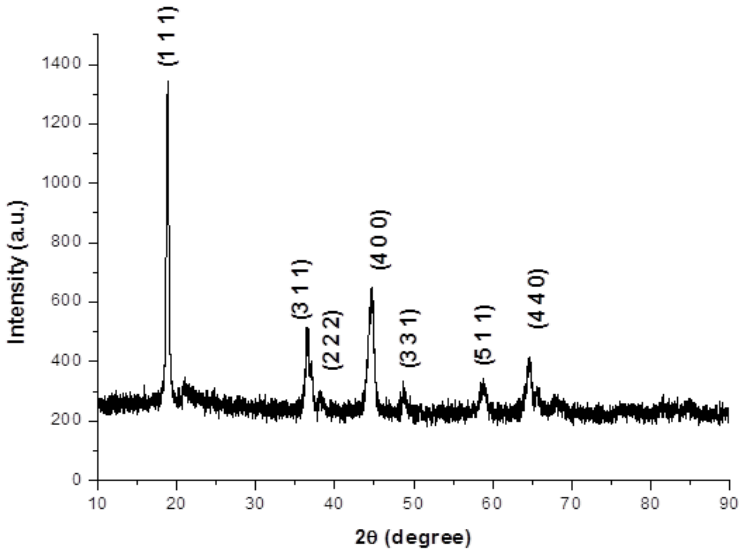

Figure 2 X-ray diffractogram of LMO after calcination at 500 °C.

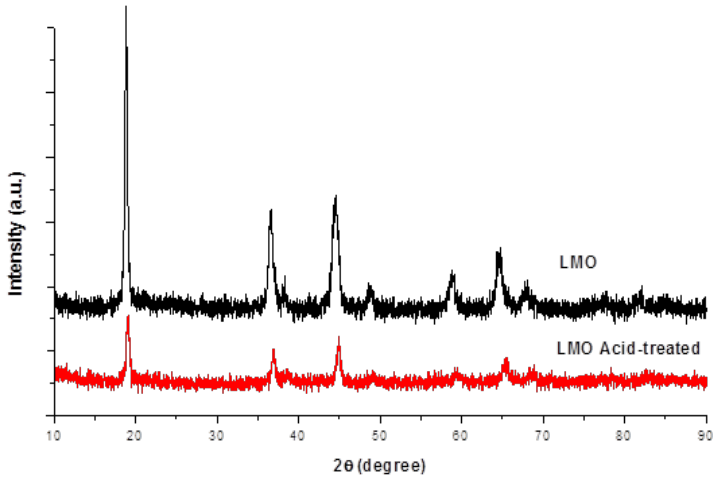

Figure 3 X-ray diffractogram of LMO before and after acid treatment, indicating peak shifts as high as 0.3725 degrees 2θ.

The possibility of peak shifting is due to the ion exchange and redox mechanism during the acid treatment process. The peak shifting can indicate that there is a change in the lattice parameter.

Table 1 Calculation results in lattice parameter before and after acid treatment.

Adsorbent	Lattice Parameter (Å)	
	Before acid treatment	After acid treatment
LMO	8.15	8.08

Table 1 shows the lattice parameter calculation of the LMO before and after the acid treatment. The lattice parameter was reduced after the acid treatment due to the ion-exchange process between Li^+ and H^+, as shown in Eq. (1). This mechanism is more desired for a better uptake of lithium due to its better ability to maintain the spinel crystal structure.

$$3Li_{1.6}Mn^{4}{}_{1.6}O_4+H^+ \rightarrow 3H_{1.6}Mn^{4+}{}_{1.6}O_4 + 4Li^+ \quad (1)$$

3.1 Lithium Uptake Analysis

The adsorption process of lithium from Lusi geothermal fluid was performed by immersing LMO into the fluid for 24 hours. An ICP test was applied to determine the content of lithium in Lusi before and after the adsorption process. This test was conducted to observe how much the adsorbent could adsorb lithium from Lusi.

Table 2 shows the results of the ICP test. It shows that LMO had successfully adsorbed lithium from Lusi. By using the formula below the lithium uptake capability for LMO adsorbent can be calculated, as shown in Table 2.

$$Lithium\ Uptake = \frac{((x-y)\times v)}{m} \quad (2)$$

x = lithium in Lusi pre adsorption (mg/liter)
y = lithium in Lusi post adsorption (mg/liter)
v = lusi volume (liter)
m = adsorbent mass (gr)

Table 2 Lithium uptake.

Adsorbent	LuSi pre adsorption (x)	LuSi post adsorption (y)	Lithium uptake (mg/g)
LMO	5.81 mg/l	5.25 mg/l	6.6

The results showed that the LMO had the ability to adsorb lithium. The absorption capability of the LMO can be attributed to the number of vacant sites in its spinel structure. These sites can attract lithium ions into the crystal structure where the manganese position is replaced by lithium.

4 Conclusions

Ion-exchange type manganese oxide LMO ($Li_{1.6}Mn_{1.6}O_4$) adsorbent was successfully synthesized through a solid-state reaction process. Lithium adsorption from Lusi could be performed using LMO-based adsorbents. The LMO had a stable spinel crystal structure. The LMO adsorbent with a crystal structure of spinel had the ability to adsorb Li as much as 6.6 mg/g. Further investigation of producing a large-capacity adsorbent powder based on the results obtained in this study will be conducted.

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