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A NOVEL PROCESS FOR RECOVERY OF KEY ELEMENTS FROM COMMERCIAL CATHODE MATERIAL OF END-OF-LIFE LITHIUM-ION BATTERY

A novel process to recover lithium and manganese oxides from a cathode material ($LiMn_2O_4$) of spent lithium-ion battery was attempted using thermal reaction with hydrogen gas at elevated temperatures. A hydrogen gas as a reducing agent was used with $LiMn_2O_4$ powder and it was found that separation of Li_2O and MnO was taken place at 1050°C. The powder after thermal process was washed away with distilled water and only lithium was dissolved in the water and manganese oxide powder left behind. It was noted that manganese oxide powder was found to be 98.20 wt.% and the lithium content in the solution was 1,928 ppm, respectively.

Keywords: Lithium manganese oxide, Cathode material, Thermal Reaction, Lithium

1. Introduction

Lithium, which is used in lithium-ion batteries, is lighter than other battery materials such as nickel, cadmium, and lead, but has high energy density. Thanks to these advantages, lithium-ion batteries are expanding their use in various fields, from electronic products such as smartphones and laptops to electric vehicles and energy storage devices. The lithium-ion battery has the advantage of not being able to discharge naturally and has a long lifespan. Based on this, recently, it is widely used in military equipment, automation systems, and aviation equipment. Lithium-ion batteries are also a key driver of the 4th industrial revolution related to drones and IoT.

The first commercialized cathode material was LCO, a layered lithium cobalt oxide developed by John B. Goodenough's lab in 1991, and the first lithium-ion was released by Sony. Since then, a spinel LMO consisting of manganese was developed through additional research to be used as a cathode material and is used for various commercial purposes. LMO is especially outstanding in terms of economic feasibility and safety and thus is partially used in lithium batteries for electric vehicles. Its energy capacity is lower than that of LCO, which is combined with NCM at a specific ratio to be used in lithium batteries for electric tools and electric vehicles, but has a structural instability as it dissolves in electrolytes when the operating temperature rises beyond 60°C [1,2]. As of 2015, the global demand for LMO is 23,941 tons, and with high growth in annual production, its demand is expected to increase more; accordingly, the importance of developing a recycling technique for waste LMO is increasing.

Spinel-type Li-Mn-O are attractive candidates for commercial lithium extraction owing to their high capacity and superior selectivity towards lithium. LiMn-O are synthesised as precursor materials, from which the ion sieves are obtained by replacing the Li^+ with H^+. Li-Mn-O can be synthesised via various methods including solid state reaction, sol-gel, hydrothermal or reflux, yielding different particle sizes and morphologies, which lead to different ion exchange capacities of the lithium de-intercalated sorbents. In general, the Li-Mn-O precursors can be expressed by the formula $(Li)[Li_xMn_{2-x}]O_4$, where A-site (mostly Li) and B-site (Li and/or Mn) represent 8a tetrahedral and 16d octahedral sites [3], and the acid treated ion sieves have a general formula of $MnO_2 \cdot xH_2O$. The primary Li uptake mechanism for the spinel-type sorbents is the Li^+/H^+ exchange, in which the Li^+ can be intercalated/ de-intercalated into the octahedral interstices, with an intact spinel structure [4]. Furthermore, the Li^+ can be cycled in and out freely within a relatively wide range of Li:Mn molar ratios [5,6], resulting in several common manganese oxide precursors including $LiMn_2O_4$ [3,5,7-11], $Li_{1.6}Mn_{1.6}O_4$ [4,12-19] and $Li_{1.33}Mn_{1.67}O_4$ [19-25]. Desorption/ regeneration of the spinel-type sorbents requires contacting the sorbents with acid.

The lithium manganese oxide, $LiMn_2O_4$, crystallises with a cubic spinel-like structure. The structural relationship between

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the spinel Li[Mn$_2$]O$_4$ and the lithium deficient materials was described by Hunter [26]. Its crystallographic structure possesses the symmetry Fd3m and has a general structural formula A[B$_2$]O$_4$, where the B cations reside on the octahedral 16d sites, the oxygen anions on the 32e sites, and the A cations occupy the tetrahedral 8a sites. The approximately cubic closepacked array of oxide ions incorporates MnO$_6$ octahedron sharing two opposing corners with LiO$_4$ tetrahedra (Fig. 1). The spinel structure is primarily characterised by structural groups as follows. (1) MnO$_6$ octahedra, connected to one another in three dimensions by edge sharing. (2) LiO$_4$ tetrahedra, sharing each of their four corners with a different MnO$_6$ unit but essentially isolated from one another. (3) a three-dimensional network of octahedral (16c) and tetrahedral (primarily 8a) sites, through which lithium ions can move through the (1Ī1) channels of the spinel lattice.
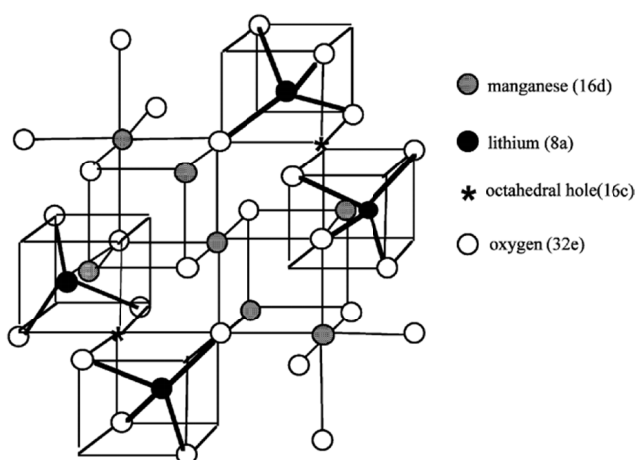

Fig. 1. Schematic representation of the spinel structure of LiMn$_2$O$_4$ [26]

There have been many studies on recovering valuable metals from waste lithium-ion batteries, and generally, the recycling process of waste lithium-ion batteries consists of mechanically disassembling batteries, chemically extracting metal, and recovering valuable metals by refining [27]. The most frequently used method in the extraction of valuable metals from separated cathode materials is acid leaching, where various studies on the effects of leaching on various acid solutions have already been conducted [28-31]. Solvent extraction after leaching can recover lithium, cobalt, nickel, manganese, etc., which many studies on the effects of recovery based on the solvent have reported as well [32].

Recovery of valuable metals from waste lithium-ion batteries through acid leaching and solvent extraction has high recovery efficiency and the recovered metal components have high purity, but byproducts from the process must be disposed of, and this requires a series of complex and massively expensive processes. Moreover, since most studies are on the first cathode material developed, LCO, few studies have yet been conducted on recovery of valuable metals from more recent cathode materials, LMO or MNC, which have better price and stability.

Therefore, a novel process was investigated with hydrogen in order to phase transformation from lithium manganese oxide at elevated temperatures. This new process was not using toxic solution studied before and this method was conducted by gas reaction and water leaching. The separation and recovery of valuable materials from the cathode was conducted on the effect of temperature and reactive gases. The phase after thermal reaction was examined by XRD(X-ray fluorescence) and their chemical composition was analyzed by ICP-OES(Inductively coupled plasma – optical emission spectrometry), respectively.

2. Materials and methods

The specimen used in the experiment was LMO powder that was physically separated from waste lithium-ion batteries. XRF (X-ray fluorescence), ICP-OES (Inductively coupled plasma – optical emission spectrometry) and XRD (X-ray diffraction) were performed to analyze raw specimens and identify the phase and chemical compositions shown in Figure 2. XRD analysis of raw specimens showed that LMO was a spinel lithium manganese oxide in the LiMn$_2$O$_4$ phase, and the composition analysis through XRF and ICP-OES analysis showed 94.89 wt.% manganese content with trace amounts of lithium (3.59 wt.%) and aluminum (1.52 wt.%).

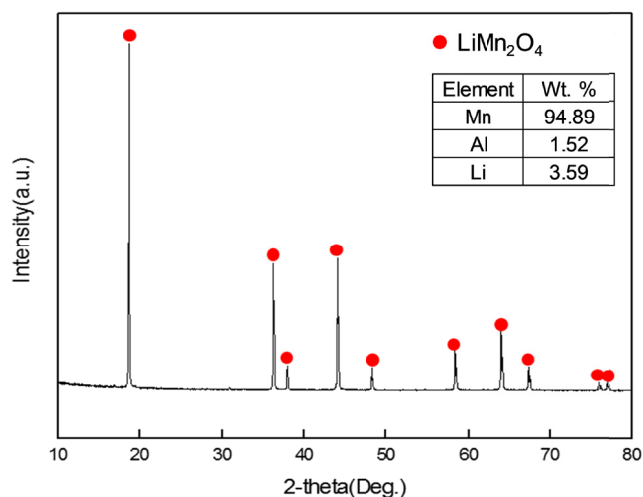| Element	Wt. %
Mn	94.89
Al	1.52
Li	3.59

Fig. 2. XRD patterns and chemical composition of cathode material from LMO battery

Separation and recovery of lithium and manganese in LMO consists of hydrogen reduction and washing. The apparatus used for hydrogen reduction was a horizontal tube furnace; Fig. 3 presents its schematic diagram. A is a SiC heater that receives electricity and causes resistance to increase the temperature inside. B is a thermocouple that measures and controls the temperature inside. C is a crucible, which in this experiment was made of aluminum and was where the specimen to be tested was placed. D is the gas bombe where the gas to be injected is appropriately positioned; Ar and H$_2$ gas were used for this experiment, and these gases were injected inside through the flow meter (F) by adjusting the amount of gas injected. E shows the placement of a water cooling tube, which minimizes deformation of equipment due to high temperature.
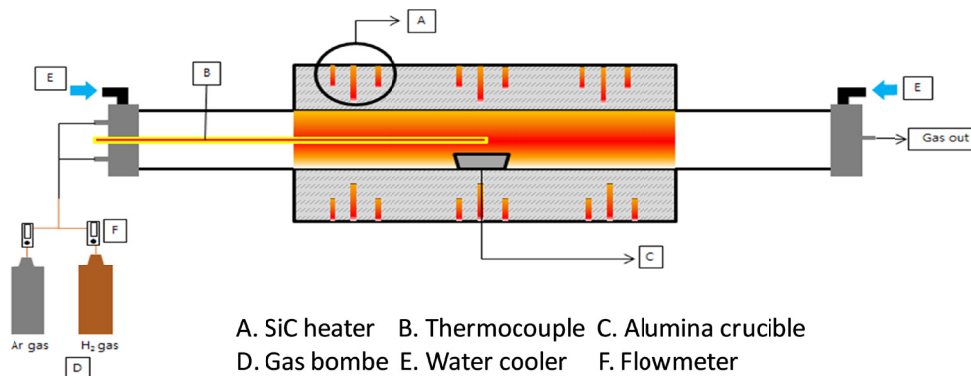
A. SiC heater   B. Thermocouple   C. Alumina crucible
D. Gas bombe   E. Water cooler   F. Flowmeter

Fig. 3. Schematic diagram of experimental apparatus

The cathode powder($LiMn_2O_4$) was placed in an alumina crucible with H_2 gas(300cc/min) at the range of temperature from 350℃ ~ 1050℃ for 1~ 3 hours. The specimen recovered after hydrogen reduction with LMO was washed by distilled water at 1/10 weight ratio, washed for 30 minutes to separate lithium and manganese. When the water washing is done, distilled water containing lithium and sludge of manganese oxide is separated by vacuum distillation method for 1 hour.

3. Results and discussion

To verify LMO reactivity at high temperature prior to thermal reaction with hydrogen experiment, TGA (thermo gravimetric analyzer) analysis was performed with temperature raised to 900℃ at 10℃/min in an air gas atmosphere to observe the weight change. The results are displayed in Fig. 4

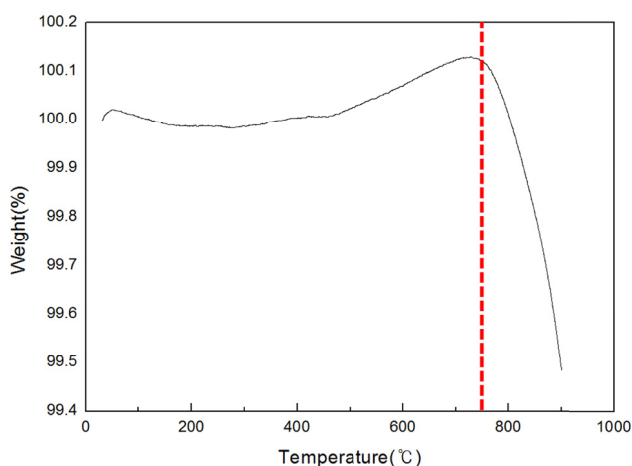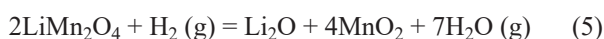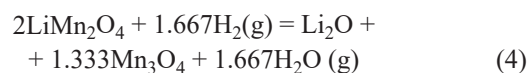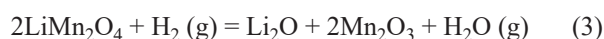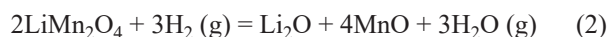Fig. 4. TGA curve of LMO according to increasing temperatures up to 990℃

As seen in the TGA analysis result, LMO showed drastic weight loss at temperatures beyond 800℃, which is presumed to be due to LMO's spinel structure becoming unstable at high temperatures and $LiMn_2O_4$ phase decomposition, losing oxygen, into either Li_2MnO_3 or $Li_{1-2a}Mn_{2-a}O_{3a-a'}$. LMO may have become active in this temperature range to have reactivity. 33)

The reaction formula is as follows:

$$LiMn_2O_4 \rightarrow aLi_2MnO_3 + Li_{1-2a}Mn_{2-a}O_{3a-a'}, + a'/2O_2 \quad (1)$$
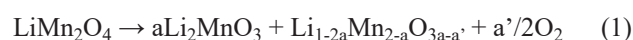
3.1. Thermal reaction with hydrogen gas (H_2)

To confirm the reactivity of the cathode material, LMO, with hydrogen, a specific amount of specimen was placed on the aluminum crucible inside the horizontal tube furnace for the reaction, and the experiment temperature ranged from 350℃ to 1050℃ to confirm reactivity. The anticipated chemical reaction formulas of LMO in hydrogen reduction were as follows:

$$2LiMn_2O_4 + 3H_2 (g) = Li_2O + 4MnO + 3H_2O (g) \quad (2)$$

$$2LiMn_2O_4 + H_2 (g) = Li_2O + 2Mn_2O_3 + H_2O (g) \quad (3)$$

$$2LiMn_2O_4 + 1.667H_2(g) = Li_2O + \\ + 1.333Mn_3O_4 + 1.667H_2O (g) \quad (4)$$

$$2LiMn_2O_4 + H_2 (g) = Li_2O + 4MnO_2 + 7H_2O (g) \quad (5)$$

Based on the above formulas, hydrogen reduction was performed for 1 hour at 350℃, and recovered powder was observed for phase change through XRD analysis, with results as in Fig. 5.
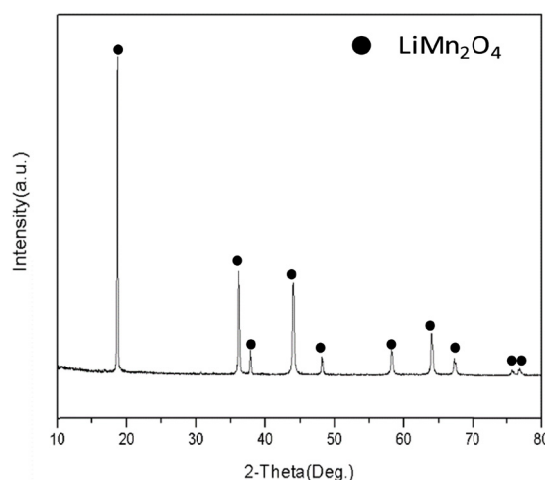

Fig. 5. XRD patterns of LMO system Li-ion battery scrap after hydrogen reduction
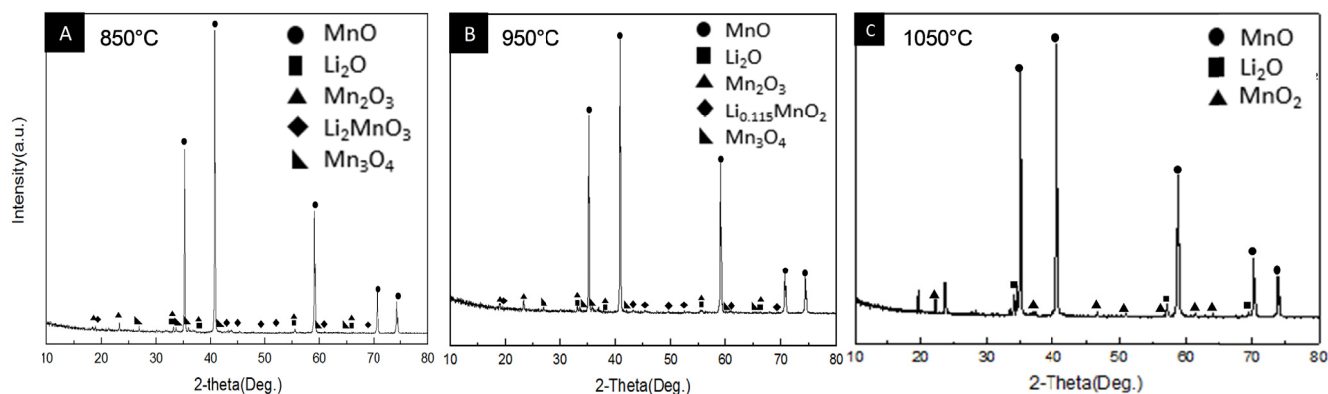
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Fig. 6. XRD patterns of LMO cathode material after hydrogen reaction at each temperature

In the hydrogen reduction of LMO at 350°C, no phase change was detected, which is presumed to be because the spinel structure is stable at low temperatures below 800°C. Therefore, as confirmed by TGA results, hydrogen reduction was performed at 850°C, 950°C, and 1050°C, where LMO was anticipated to become active, for 3 hours. Results of XRD analysis appear in Fig. 6.

As seen above, phase separation between lithium and manganese oxide occurred when hydrogen reduction was performed at 850 and 950°C for 3 hours. However, at 850 and 950°C, there were still undecomposed lithium manganese oxides such as Li_2MnO_3 or $Li_{0.115}MnO_2$, confirming that a complete separation of lithium and manganese oxide did not occur. On the other hand, after 3 hours of hydrogen reduction at 1050°C, no lithium manganese oxide was observed, and only lithium oxide and manganese oxide were observed, confirming that complete LMO separation occurred at 1050°C.

The solubility difference between two powders was used in order to separate lithium oxide and manganese oxide from the powder mixture of manganese oxide and lithium oxide through hydrogen reduction. Whereas manganese oxide is insoluble in water, lithium oxide reacts with water and dissolves in water as it turns into lithium hydroxide as in the following formula:

$$Li_2O + H_2O_{(l)} \rightarrow 2\ LiOH_{(aq)} \qquad (6)$$

Based on this property difference, the hydrogen-reduced LMO powder was mixed with distilled water at 1/10 weight ratio, washed for 30 minutes, and filtrated to separate liquid and powder; recovered liquid was used for ICP analysis to confirm the lithium content, and powder was used for XRD analysis to confirm the separation of lithium oxide and manganese oxide (Fig. 7). Unfortunately, there are peaks such as aluminum and lithium found by XRD and it can be explained that aluminum came from an original specimen and lithium was not dissolved by water completely and remained with the powder. SEM analysis was performed to confirm the particle size and shape of recovered powder (Fig. 7).

Only MnO was observed during XRD analysis of the recovered powder, confirming that lithium oxide and manganese oxide separated after washing. The manganese content in recovered
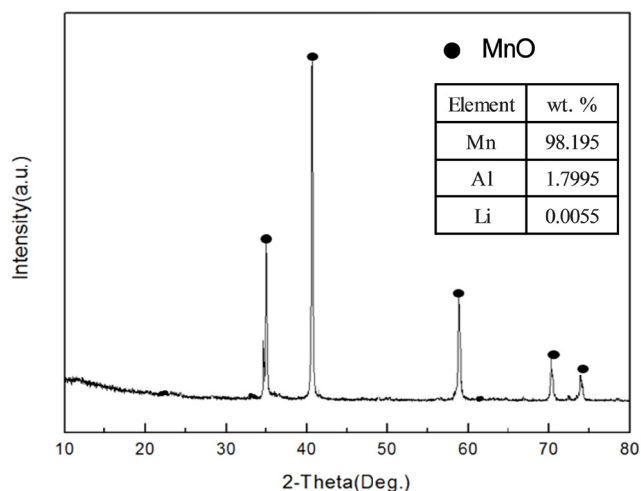

Fig. 7. XRD patterns and chemical composition of residue after water leaching

powder was found through XRD analysis to be 98.20 wt.%, with 1.80 wt.% of Al and 0.006 wt.% of lithium remaining, and the particle size of 10-100 μm was confirmed through SEM images. Whereas manganese oxide is insoluble in water, lithium oxide can dissolve in water as it turns into lithium hydroxide. The recovered water containing lithium was examined by ICP and it was found to be a lithium concentration of 1,928 ppm.

4. Conclusions

An experiment on lithium and manganese separation of cathode material in LMO from lithium-ion batteries was conducted through hydrogen reduction, and the results were as follows:

1. Phase separation between lithium and manganese in LMO due to hydrogen reduction reaction occurs at temperatures beyond 800°C, and complete separation into lithium oxide and manganese oxide occurs after 3 hours of reaction at 1050°C.

2. Separation of lithium oxide and manganese oxide was possible through washing, and complete separation was possible when washed for 30 minutes at a ratio of 10:1 for distilled water to specimen.
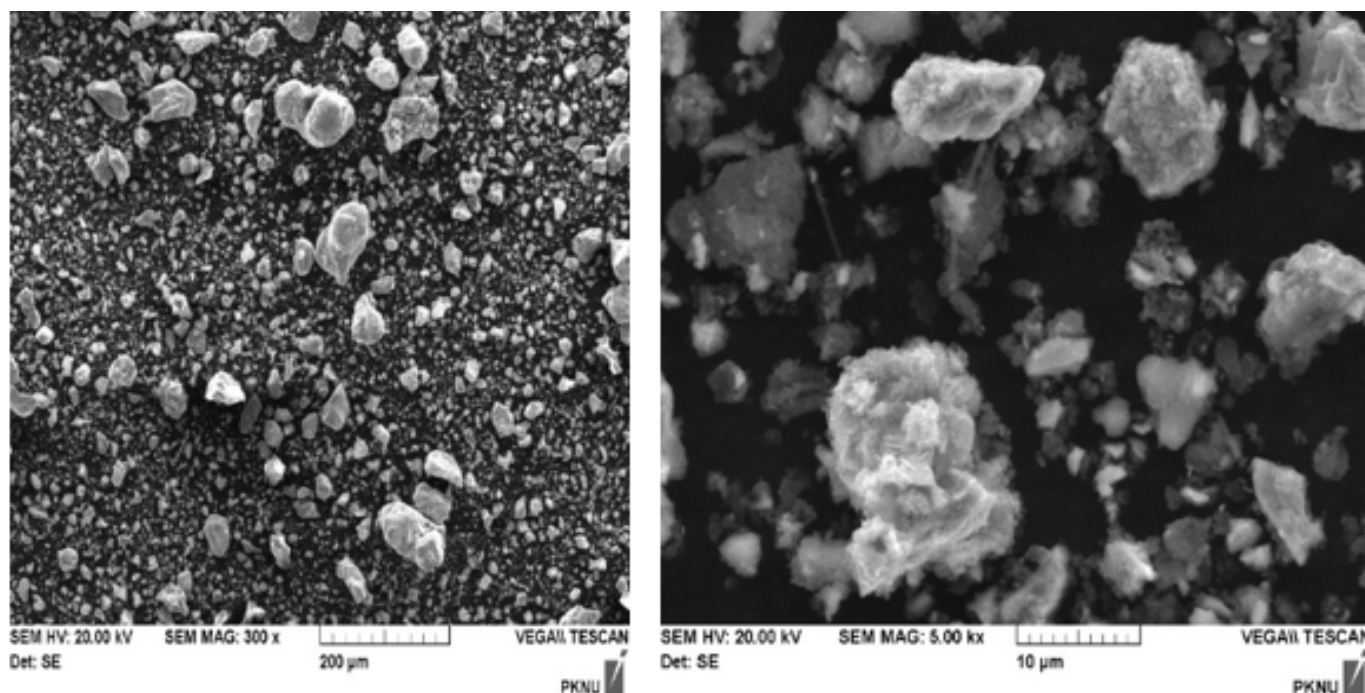
Fig. 8. SEM images of MnO powder after water leaching

3. Manganese content in manganese oxide powder that was recovered through hydrogen reduction and washing of LMO was 98.20%, and 1928ppm of lithium existed in distilled water after washing.

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